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THE LIFE AND WORK OF NIKOLAI ALEKSANDROVICH PRILEZHAEV

A. A. Akhrem, E. E. Prilezhaeva and A. P. Meshcheryakov

Nikolai Aleksandrovich Prilezhaev was born on September 28 (15), 1872 in the village of Koposevo (province of Nizhegorodskaya) into the family of a poor village priest.

He received his secondary education in the Nizhegorodskaya Ecclesiastical Semlnary, and only after the death of his father, who had destined him for holy orders, could he devote himself to the task he had set himself -- the study of the natural sciences.

After passing the examinations for the matriculation certificate and the entrance examinations, he was accepted for the science department of the physicomathematical faculty of Warsaw University (the finishing ecclesiastical seminaries at that time existed only at the universities of Tomsk and Warsaw). Here he soon became one of the students of the celebrated Russian chemist, Egor Egorovich Vagner, and while still a student he published his first scientific paper on "the nitrosates of the olefinic hydrocarbons" (1899).

After completing his course at the university he was invited by Vagner to take up the position of "laboratory steward" (equivalent to the present-day lecture assistant) in the department of organic chemistry of the Warsaw Polytechnic Institute. Over a period of years he devoted himself with perseverance and enthusiasm to the work in the laboratory and published a series of scientific papers partly connected with the studies of E. E. Vagner. The most interesting of these were "The action of acetic anhydride on diisobutene glycol" and "Oxoctenol". In 1909 his work was crowned by the discovery of what is known as the Prilezhaev reaction (the action of organic hydroperoxides on unsaturated compounds). His development of this fruitful field was recognized by the presentation of the A. M. Butlerov Prize (1912) and by his defense of a magisterial dissertation at Petersburg University (1912). Immediately afterwards he was appointed professor adjunct in the chemistry department of Warsaw University.

In 1915 N. A. Prilezhaev was invited to the Kiev Polytechnic Institute to occupy the chair of organic chemistry, and he worked there until 1924. N. A. was the first rector of the Polytechnic Institute immediately after the establishment of the Soviet regime in Kiev, and he was also dean of the chemical department of this institute for many years. In 1924 N. A. Prilezhaev moved to Minsk where he was one of the organizers both of the chemical faculty of the Belorussian State University and of the separate chemical faculty of the Belorussian Polytechnic Institute. The whole of the time he was engaged in great and diverse pedagogic activity, delivering lectures on organic, technical and biological chemistry. He took an active part in the organization of the Belorussian Academy of Sciences and was the first director of the chemical institute. During the same period N. A. Prilezhaev directed the scientific research of numerous students in the various scientific institutes of Minsk. At the same time he acted as consultant to a series of chemical institutes and enterprises in Belorussia and engaged in multifarious social activities. He participated in the work of the VSNKh, was a deputy of the Minsk Municipal Council and chairman of the Minsk division of the All-Union Mendeleev Chemical Society.

In 1933 N. A. was elected a corresponding member of the Academy of Sciences of the USSR, and in 1940 he became an actual member of the Academy of Sciences of the Belorussian SSR.

During the Great Patriotic War, N. A. Prilezhaev was energetically associated, in spite of his advanced years, with the re-establishment of the Academy of Sciences of the Belorussian SSR and of the chemical faculty of the Belorussian State University which had been transferred to Moscow. He also took part in the work of the committee for preliminary planning of the postwar development of the chemical industry of the Belorussian SSR.

Nikolai Aleksandrovich Prilezhaev passed away in Moscow on May 26, 1944 after a long and heavy illness, without being able to rejoice in the liberation of Belorussia from the fascist hordes.

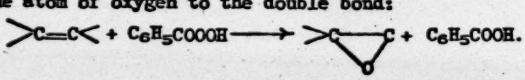
Throughout his life, which was occupied with manysided and arduous work, Nikolai Aleksandrovich proved himself a patriot of his country and great fatherland.

The scientific activity of N. A. Prilezhaev was bound up mainly with the study of the oxidation reaction and was a continuation and development of the investigations of the Russian school of chemists, notably of E. E. Vagner. Oxidation reactions, in the wider sense of processes taking place in the living organism, interested N. A. throughout his life.

In this sense the scientific work of N. A. linked up directly with the now generally accepted peroxide theory of slow oxidation by activated molecules of oxygen, which was announced in 1897 by the Russian chemist, A. N. Bakh. According to this theory peroxides are the initial products of oxidation and are carriers of active oxygen.

The researches of N. A. Prilezhaev, devoted to the interaction of organic peroxides with unsaturated compounds, threw additional light on the mechanism of the oxidation reaction and of autoxidation with molecular oxygen.

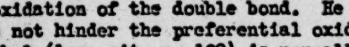
These classical investigations of N. A. were presented in a series of papers (1909-1915) and in a monograph on "Organic peroxides and their application to the oxidation of unsaturated compounds" (Warsaw, 1912). N. A. there described his new and original method of preparation of α-oxides of olefins, based on the direct oxidation of the double bond with peroxybenzoic acid. This reaction, which became known as the Prilezhaev reaction, proceeds smoothly and gives a quantitative yield of the corresponding α-oxides. On the basis of his own experimental material on the oxidation of variously substituted olefins, such as octene, the two isomers of diisobutene, decene, tetramethylethylene and dimethylcyclohexene, N. A. Prilezhaev arrived at the conclusion that the reaction between olefinic hydrocarbons and peroxybenzoic acid is accompanied by addition of one atom of oxygen to the double bond:



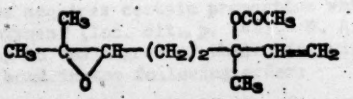
In this process the rate of oxidation of hydrocarbons by peroxybenzoic acid is dependent on the type of double bond. It falls off as a rule in passing from ditertiary olefins (containing the >C=C< group) to those with a terminal double bond >C=CH$_2$) (loc. cit., p. 99). The excess of hydroperoxide does not enter into reaction. Peroxybenzoic acid, as N. A. Prilezhaev showed, is not capable of breaking down the molecule of hydrocarbon, as is the case with other oxidation methods. It is therefore a trustworthy reagent for the qualitative and quantitative determination of the double bond in hydrocarbons of the C_nH_{2n} series. Researches by other authors on this problem, performed subsequently (S. S. Nametkin, Meerwein, Boeseken and others), fully confirmed Prilezhaev's conclusions. Thanks to the

discovery of Prilezhaev, the α-oxides and diverse products of their transformation have become readily accessible compounds.

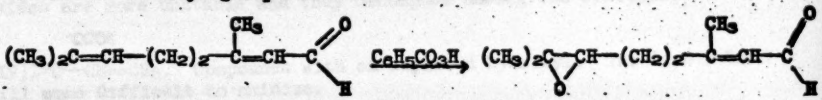
Prilezhaev was the first to direct attention to the effect of the nature of the substituent and the structure of the unsaturated compound upon the ease of oxidation of the double bond. He established that the primary alcohol group does not hinder the preferential oxidation of the double bond. Thus allyl alcohol (loc. cit., p. 102) is normally oxidized to the corresponding oxide -- glycide:



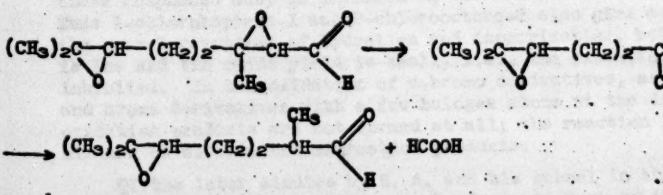
On the basis of work with geraniol and linalool (loc. cit., p. 123), which were oxidized to the corresponding mono- and dioxide, N. A. Prilezhaev showed that the double bond of the alcohol more remote from the hydroxyl group is preferentially oxidized. It transpired that the oxide ring in the α,β-position to the carbon bearing the hydroxyl group possesses a lower activity and is not susceptible, for instance, to hydrolysis by acidified water. As was demonstrated by Prilezhaev, the double bond conjugated with an acetylated hydroxyl is oxidized by peroxybenzoic acid with great difficulty. Thus in the oxidation of linalool acetate (loc. cit., p. 131) N. A. only succeeded in isolating a monoxide with the following structure:



Unsaturated aldehydes and ketones containing an isolated double bond, as for example citronellal (loc. cit., p. 104) and methyl pentenone (loc. cit., p. 108), are normally oxidized to the corresponding oxides. Unsaturated aldehydes containing, in addition to an isolated double bond, a conjugated double bond (e. g. citral) are readily oxidized to monoxides. Here the unconjugated double bond remote from the carbonyl group enters into reaction:

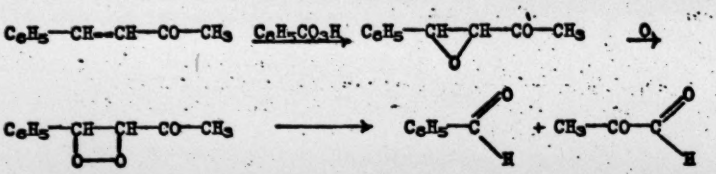


Prolonged oxidation of citral (loc. cit. p. 134) with an excess of hydroperoxide yielded, in addition to the expected citral dioxide, an aldehydo oxide containing one carbon atom less. Prilezhaev explained this phenomenon by isomerization of the aldehydo oxide into an α-keto aldehyde and breakdown of the latter into aldehydo oxide and formic acid according to the equation:



N. A. Prilezhaev showed that α-unsaturated ketones of the general formula RCH=CH—COR are oxidized by peroxybenzoic acid according to the general scheme, but the resultant α-ketoxides are extremely unstable and are therefore at once oxidized with cleavage into two molecules of aldehyde. During the oxidation of benzylidene acetone (loc. cit. p. 143) Prilezhaev obtained a small quantity of α-ketoxide. He ascribed the low yield of α-ketoxide to the ease with which it is

further oxidized under the reaction conditions according to the equation:



"....With increasing number of oxygen atoms attached to the carbon atom in the α,β-position to the double bond, oxidation is entirely suppressed" (loc. cit., p. 146). Prilezhaev failed, for instance, to oxidize cinnamic acid.

N. A. Prilezhaev had thus subdivided all unsaturated compounds into two groups in respect of their behavior with peroxybenzoic acid: 1) Compounds containing unconjugated double bonds and reacting normally with quantitative formation of oxide; 2) compounds containing for the most part a conjugated system of double bonds: "....all those in which is to be discerned either the mutual influence of double bonds or that of a double bond and some other group of atoms. As we know, such a mutual effect is most typically manifested in compounds with a conjugated system of double bonds. During the oxidation of such compounds the oxygen falling within the sphere of influence of these groups and bonds acquires certain properties which deviate from the normal properties of oxygen" (loc. cit., p. 148). N. A. Prilezhaev classifies oxygen groups according to the degree of their hindering effect upon the oxidation of the α-β double bond in the following order:

I) >COH—CH=CH_2, >C—CH—CH_2OH. Compounds of this type are oxidized normally but their oxide oxygen is inert.

II) —CH=CH—CO—CH_3—α,β-Unsaturated ketones. Compounds of this type form unstable oxides which decompose to yield aldehydes.

III) >C=CH—C(=O)H —α,β-Unsaturated aldehydes. In compounds of this type the oxides are more unstable and they decompose during the reaction.

IV) >C(OCOR)—CH=CH_2. Compounds with an acylated hydroxyl. The double bond is still more difficult to oxidize.

V) >C=CH—COOH—α,β-Unsaturated acids. The carboxyl group exercises the maximum inhibiting effect upon the oxidation of the double bond.

The later investigations of N. A. Prilezhaev and his students on the oxidation of olefinic compounds with a halogen at the double bond showed that these compounds must be included in the second of the above-enumerated classes. Thus 1-chloroheptene-1 and 2-chlorooctene-2 also give α-halo-oxides capable of the normal reactions of hydration and isomerization, but the reaction velocity is low and the oxide yield is small, i.e., the oxidation of the double bond is inhibited. In the oxidation of α-bromo derivatives, as well as of polychloro and bromo derivatives with a few halogen atoms at the double bond, normal oxidation products are not formed at all; the reaction leads to a complex mixture of diverse transformation products.

Of the later studies by N. A. and his school in the field of oxidation with peroxybenzoic acid, attention may be drawn to work on the oxidation of some terpen derivatives, as well as on amines and their mixtures. In the later years researcl was started on the mechanism of bromination of tertiary alcohols, likewise a stud

of the Grignard reaction with halo derivatives containing a halogen at the double bond [1]. A series of papers by Prilezhaev and his students was lost in manuscript form at the start of the Great Patriotic War.

Prilezhaev's classical investigations on the oxidation of unsaturated compounds stimulated a large number of researches on β-oxides during the last forty years both in this country and abroad. These investigations fully confirmed the conclusions of Prilezhaev concerning the velocities of oxidation of variously substituted double bonds and concerning the inhibiting effect of the carbonyl, ester and carboxyl groups on the oxidizability of the double bond.

"Prilezhaev's law" proved to be much more important and more widely applicable than even its author had postulated. Thus it has recently been discovered to apply also to the oxidation of unsaturated compounds with potassium permanganate, chromic acid mixture and atmospheric oxygen (Bartlett [2], Howard [3], A. P. Meshcheryakov [4] and others). In all these cases ditertiary olefinic compounds are oxidized at a rate many times greater than the velocity of oxidation of less highly branched hydrocarbons, thus pointing to similar or identical mechanisms of reaction. This problem has great technical importance, for instance in connection with the necessity for control of processes taking place during storage in the air of high-grade fuels containing a high percentage of branched olefins. Polymerization of lower olefins in presence of air likewise leads to formation of a considerable amount of readily oxidizable branched olefins.

It must be noted that the majority of papers by foreign authors on problems of oxidation of olefinic compounds deliberately ignore the priority of Russian science in this important field of organic chemistry. The following examples are far from exhaustive: The above-mentioned papers of Bartlett [2] and Howard [3], also the paper of Swern [5] which gives the correct electronic interpretation of the mechanism and characteristics of the reaction of oxidation of double bonds by hydroperoxides. Acknowledgment to N. A. is only made in respect of one detail and the fact is completely ignored that the law now formulated had been described by him in full as far back as 1912. This omission also applies to some papers by Russian authors. The present short paper is intended to direct the attention of the Soviet scientific community to the chemical heritage of the Russian classical organic chemist, Nikolai Aleksandrov Prilezhaev.

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NUCLEAR PERIODICITY OF THE MENDELEEV TYPE

E. P. Ozhigov

Mendeleev's periodic law, one of the fundamental laws of nature, constitutes the theoretical foundation of modern chemistry. It reflects not only the electronic structure of the atom but also the periodic properties of the atomic nucleus, and in this sense is one of the most important and profound laws of nature.

As S. A. Shchukarev showed in his later studies [1,2], behind the apparently arbitrary ratios of atomic weights is concealed a complex nuclear periodicity, a fact which had been glimpsed by the creator of the periodic system himself. Nevertheless the modern version of the periodic law in the periodic system is incomplete, since it is mainly associated with the charge and electronic structure of the atom but not with its mass, and the latter is regarded as a secondary and concomitant characteristic of an element.

The properties of the atomic nuclei, manifested in the existence of numerous isotopes, in odd- and even-number periodicity of elements, in the empirical laws of existence of isotopes (e.g. the Shchukarev-Mattauch and Aston laws), are not explained by the periodic system and therefore do not fit into the framework of the latter. This situation has arisen because the individual forms of nuclear periodicity have been insufficiently investigated while periodicity of the Mendeleev type has scarcely been discussed in the literature.

In the present paper the author describes his experiment on the construction of a system of the pleiads of natural isotopes which graphically takes into account the known forms of nuclear periodicity and, in particular, periodicity of the Mendeleev type. The work was carried out at the end of 1942 and presented in a short communication a little later [3].

The guiding philosophic impulse to this investigation was given by I. V. Stalin's statement that "....movement has a double form: evolutionary and periodic"; and later: "concerning the forms of movement, concerning the fact that, according to dialectics, small qualitative changes ultimately lead to large quantitative changes, the same law applies with equal force to the story of nature." I. V. Stalin later, in a general form, without analyzing the specially quantitative and qualitative forms of movement, emphasizes that "the Mendeleev periodic system of the elements clearly demonstrates the great importance in nature of the development of qualitative changes from quantitative changes" [4].

Mendeleev himself also recognized the revolutionary role of change in the development of the elements. According to him: "The periods of the elements are points, numbers, gaps, masses, and not a continuous development" [5]. In Mendeleev's work we see in rudimentary form an attempt to take also into account the evolutionary aspect of the development of the elements, as when he observed the similarity in chemical properties of elements with similar atomic weights. Modern knowledge of the isotopic composition of the elements, unknown in Mendeleev's time, reveals the evolutionary pattern in the development of any given element; each element comprises a series of isotopes with increasing mass numbers, but with similar chemical properties of the isotopes with the same nuclear charge. Revolutionary jumps occur in transition from the pleiads of isotopes of one element to the pleiads of isotopes of other elements.

Such an approach leads to the necessity for studying the series of natural isotopes and the interrelations between them. Nuclear periodicity of the Mendeleev type is readily recognized in the natural series of isotopes if we make use of the principles applied by Mendeleev in the creation of his inspired periodic system:

a) Arrange isotopes in the order of increasing mass numbers.
b) Arrange the isotopic series vertically in accordance with the teaching of D. I. Mendeleev on element-analogs.

The author has proposed a modified short table for stable and partially radioactive isotopes (including also the artificial isotopes) which is so arranged as to be complete. The short form was selected because it brings out more readily the relation between nuclear periodicity and chemical periodicity. The radioactive isotopes were included with the aim of establishing generalizations concerning their distribution among the stable isotopes. In the table of isotopes of elements the odd numbers are given in the form of squares; pleiads of isotopes of even numbers are in the form of sloping parallelograms arranged one after the other in the case of isobars.

The isotopes of greatest percent abundance in a pleiad of elements are shaded throughout the whole area corresponding to the given isotope; isotopes of least percent abundance are shown in the form of shaded triangles.

The system of pleiads of isotopes is reminiscent in appearance of the usual form of Mendeleev table; it reflects the chemical relationship between the elements. Such a system, however, reflecting the presence of isotopes, their quantity and position in the periodic system, will reflect in large measure the periodicity of the atomic nuclei. Graphically it distinguishes the following forms of periodicity:

1) Periodicity of even and odd atomic numbers.

2) Mendeleev periodicity.

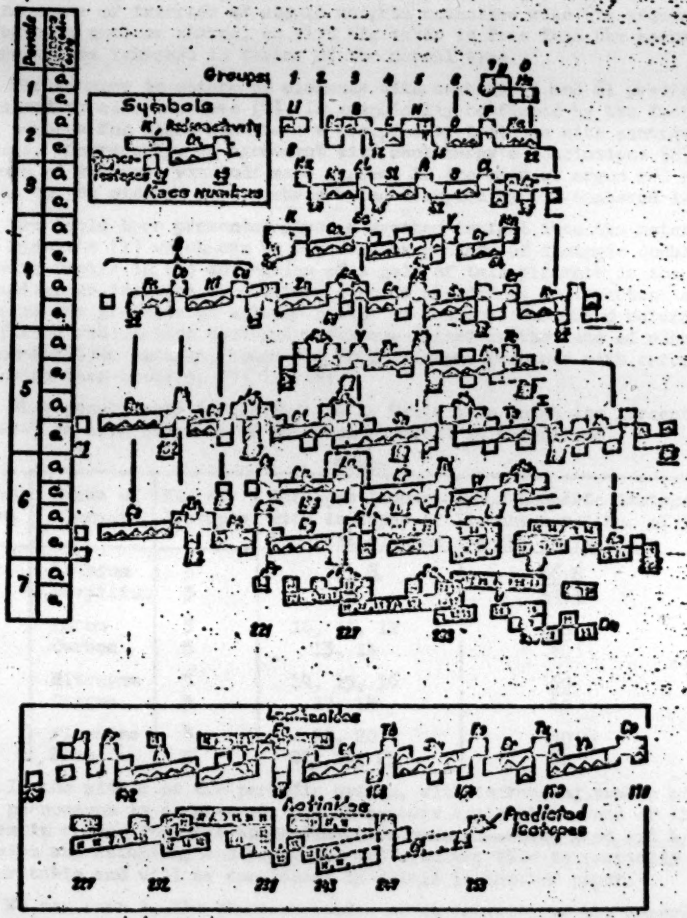
3) Periodicity associated with regular changes of position of the principal isotopes (isotopes of greatest percent abundance or isotopes with the longest life period) in the pleiads.

The first form of periodicity is associated with the continuous series of isotopes, concepts about which were formerly applied to explaining the absence of certain elements in nature [2,6,7], but in the present case are for the first time distributed throughout the whole system of elements. Odd-numbered isotopes are raised up a little on the diagram to differentiate them from the even-numbered isotopes and to bring out a series of empirical regularities in their distribution. (The Shchukarev-Kattauch law and exceptions therefrom, the Aston law, etc.).

According to the Shchukarev-Kattauch law there does not exist a single pair of stable isotopes the charges on which could differ only by one unit. This rule is illustrated in our table by means of "gaps" in the series of the even-numbered isotopes the mass numbers of which belong to the odd-numbered element series. Under the same conditions, when exceptions occur (the pairs: $^{113}_{48}$Cd and $^{113}_{49}$In; $^{115}_{49}$In and $^{115}_{50}$Sn; $^{123}_{51}$Sb and $^{123}_{52}$Te; $^{187}_{75}$Re and $^{187}_{76}$Os) or in the case of the radioactive isotope $^{40}_{19}$K and the inactive $^{40}_{20}$Ca, etc., this is represented on the diagram by paired vertical duplication of the isotopes.

The Aston law states that to each odd number z corresponds only one or two isotopes; when two isotopes are present their mass numbers are always odd and differ by 2. There are four exceptions: $z = 1,3,5,7$. This rule is expressed with exceptional clarity in the table, likewise other rules for isotopic

Periodic System of Pleiads of Isotopes



distribution including the rule for known isotopes with even numbers. The pleiads are distributed regularly one after the other, corresponding to the ordinal numbers of the elements.

We see from the table that anomalies in the atomic weights are caused by breaches in the regular order of distribution of the isotopes of greatest percentage abundance (Ar and K, Co and Ni, Te and I, Th and Pa). The table graphically expresses the rule discovered by Grosse [8] which states that the sequence of increase of atomic weights coincides with the sequence of the increase in nuclear charge, so that the table is free from the anomalies and discrepancies inherent in tables of the normal type.

The absence in nature of elements with numbers 43 and 61 previously explained by other authors [7], is graphically confirmed by the fact that the mass numbers for these numbers are occupied by isotopes with contiguous even numbers. Conversely, in agreement with Shchukarev's conclusions [2] the absence of isotopes with odd mass numbers in the case of argon and cerium is due to the missing mass numbers being occupied by odd-numbered isotopes.

The table here presented gives a greater insight into the nature of twin elements [1] which can be regarded as pleiads of isotopic doublets. The decisive factor in the definition of a pair of twin elements is the presence of contiguous isotopes of greatest percent abundance; an important characteristic is the presence of a large number of isobars including natural and artificial radioactive isotopes which are formed in the case of elements of odd number (for example, boron has 100% isotopes isobaric with carbon of the following mass numbers: 10, 11, 12).

This peculiarity is illustrated by Table 1 in which the percentage of isobars in twin elements of the second period is underlined.

Table 1

Ordinal Nos.	Names of Elements	No. of Isotopes	Isotopes isobaric with isotopes of the next element	% of isobaric isotopes in the total No. of isotopes in the pleiads
3	Lithium	3	7, 8	66.6
4	Beryllium	3	10	33.3
5	Boron	3	10, 11, 12	100
6	Carbon	5	13, 14	40
7	Nitrogen	5	14, 15, 16	60
8	Oxygen	5	17, 18	40
9	Fluorine	4	19, 20	50
10	Neon	5	21, 22, 23	60

In the middle of the periodic system, with increasing number of isobars, this phenomenon is suppressed, but it appears again at the end of the periodic system in connection with the radioactive twin elements: lead and bismuth, polonium and astatium, and neptunium and uranium; this is partially illustrated in our table and will be considered in detail in another paper.

We now turn to the characteristics of periodicity of the Mendeleev type. A number of authors have pointed to the possibility of a periodicity of the atomic nucleus similar to the periodicity of its electronic structure. According to Fersman [9] we may "...anticipate the possibility of detecting in the nucleus a certain periodicity resembling the periodicity of the Mendeleev table."

In his later papers S.A.Shchukarev makes more detailed and lucid predictions of the existence of such a form of periodicity.

One of his suggestions characteristically takes the following form: "...large transitions of masses are, as it were, periodically repeated in the case of a series of chemical analogs; this is illustrated, for instance, by transitions from halogens to inert gases; from As and Sb to S and Te; from Zn and Hg to Ga and Tl. It is true that in these examples periodicity of the Mendeleev type (i.e. with the classical long periods) is not so conspicuous as in the theory of electronic shells, but it is nevertheless permissible to advance the hypothesis that it exists even though in a disguised form" [1].

The proposed system of isotopic pleiads not only provides a clear representation of this nuclear periodicity but also reveals the existence of some quantitative regularities. One of these was observed by Mendeleev himself and relates to the regular change in the magnitudes of the differences in atomic weights of elements of chemical analogs.

"The magnitude of the atomic weight of elements belonging to neighboring large periods differ, by approximately 45, for example K—Rb, Cr—Mo, Br—I, but the elements of a typical series have a smaller difference of atomic weight. The difference between the atomic weights of Li, Na and K is equal or close to 16, that between Ca—Mg and Ba is the same, that between Si and C is 16.1, that between S and O is 16.06, and that between Cl and F is 16.45. With increasing atomic weight the elements of one of two neighboring (small) series generally have a large difference (about 20 = Ti—Si = V—P = Cr—S = Mn—Cl = Fb—As, etc.). The difference reaches a maximum in the heaviest elements: Th—Pb = 26; Bi—Ta = 26; Ra—Cd = 25, etc.

"Consequently, a relation with change of properties, even though obscure, is to be observed in the magnitudes of the atomic weights of analogs" [10].

Aston [11] later attempted to correlate the periodic properties of atomic nuclei of elements with their chemical manifestations. He wrote: "The study of stable isotopes has revealed only one well-defined periodicity: the limiting numbers of the isotopes of the odd elements. Examination of the table of mass numbers shows that many cases exist where a mass number difference of 44 is associated with an atomic number difference of 18. These differences link the atoms with analogous chemical properties, such as $_{35}Cl$, $_{179}Br$. Similarly a difference of 88 is associated with a corresponding difference of 32, as $_{93}Nb$, $_{181}Ta$".

Aston's tables, however, do not reflect this dependence.

Our analysis of the continuous isotopes showed that at the nodal points of the system along the vertical lines there is a difference in the mass numbers of the second and third periods of 16; that between the fourth and fifth is 44-48; and that between the sixth and seventh is 88-90. These nodal points enabled the series of isotopes of the respective periods to be arranged one below the other. Incidentally we may note that in some instances these points link the nuclei of single-type structure in the helio group, for instance $_{16}O$ and $_{32}S$, $_{17}O$ and $_{33}S$, etc. This regularity admittedly becomes complicated on transition to the remaining periods with increasing numbers of neutrons in the nuclei.

It is interesting to note that the difference between the vertical periods coincides with the difference between the horizontal periods.

The difference in the atomic numbers of the corresponding short and long periods (up to the start of the isotopes of the following period) is approximately uniform and forms the series: 4, 16, 16, 45, 46, 90 (calculating up to the mass

number 221 belonging to element number 87), although the length of each succeeding period in comparison with the preceding one is somewhat larger.

The "attenuation" of mass observed by S. A. Shchukarev in some parts of the periodic system is confirmed. In our table this is reflected in a lengthening of the pleiads of isotopes on the right side of the periodic system.

Hence nuclear periodicity of the Mendeleev type is manifested not only in the general character of the distribution of isotopes into groups, which is reminiscent of the arrangement of the elements in tables of the conventional type, but also in the presence of certain nodal points common to both systems. The Mendeleev difference in the magnitude of the atomic weights of analogs is paralleled by the difference in the mass numbers of isotopic analogs. The genetic relation between the Mendeleev system and the system of pleiads of isotopes is illustrated by Table 2.

A striking feature is the symmetry of the isotopic system, due to each element constituting an isotopic period in the transition of the nuclear mass from plus to minus activity.

The highest concentration of mass falls on the isotopes of greatest percentage abundance. Notwithstanding the difference of the number of isotopes in the short and long periods, the main isotopes (especially in the case of odd elements) are approximately equally spaced, and this results in the appearance of chemical isotope-analogs in the corresponding groups of elements. As an example we may cite the periodicity of the pleiads of isotopes of the second and third short periods. The range of each period in mass numbers is identical. The pleiads are arranged one below the other in conformity with the laws of Shchukarev, Aston and others, while isotopes possessing similar nuclear structure also have similar values of nuclear spin ($_{7}Li$ and $_{23}Na$, $_{11}B$ and $_{27}Al$, $_{15}N$ and $_{31}P$, $_{16}O$ and $_{32}S$, $_{19}F$ and $_{35}Cl$, etc.).

The difference in mass numbers of analogs is 16 and in the majority of cases it applies to the chemical analogs.

In addition there are isotopes in which the atomic difference of 16 is not associated with repetition of chemical properties ($_{10}B$ - $_{26}Mg$, $_{14}N$ - $_{30}S$, $_{21}Sc$ - $_{37}Cl$). However, these exceptions, even though concealed, do not upset the general rule.

In the doublet series of the isotopes of long-period elements there is no full similarity, and therefore the series are displaced in relation to each other, thereby, as it were, emphasizing their chemical dissimilarity.

It is important to note that corresponding to the laws of distribution of the natural isotopes is the law of distribution of the radioactive ones, including the artificial isotopes with the longest life. Thus, below $_{55}Mn$ appears its complete analog $_{89}Tc$ (the difference in the ordinal number is 18, the difference in mass numbers is 44), with a half-life period of 4.10^{6} years.

Special interest is presented by an analysis of the final portion of the periodic system, since it then becomes possible to predict the still undiscovered isotopes of the transuranium elements. The difference in mass numbers of 88 is the dominating factor in the construction of the lanthanide and actinide series.

Under this condition, below the pleiad of element no. 55 and the expected isotope $_{133}Cs$ appears the pleiad of element no. 87 with the first isotope $_{221}Fr$. The latter pleiads of isotopes are arranged one below the other. In some cases a difference occurs in the mass number difference of the isotope-analogs; e.g.

Table 2

Periods	Range in mass nos. up to the start of the next period	Difference between the periods in the vertical direction in units of atomic wt.		
		Name	According to Mendeleev	According to table of isotopes
1	4	Between 2nd and 3rd periods	16	16
2	16			
3	16			
4	45	Between 4th and 5th periods	45	44—48
5	46			
6	90	Between 6th and 7th periods	90	88—90

the isotopes $_{231}Pa$ and $_{141}Pr$ have a difference of 90.

Corresponding to the development of radioactivity in a given region of the series of lanthanides is a region of maximum radioactive disintegration of actinides. To a part of the radioactivity of samarium and element no. 61 corresponds the development of the group of transuranium elements, starting from no. 93.

The pleiad of curium isotopes (no. 96) is represented at present by two isotopes with mass numbers 240 and 242. Starting from the periodicity of the pleiads of isotopes of gadolinium and curium and the difference of 88-90, it is necessary to complete the pleiad of curium isotopes by the isotopes 243, 244, 245, 246, and 248, representing the series of isotopes predicted by Seaborg [12].

Similarly, for element no. 97, by adding to the atomic weight of Tb (159.2) the differences of 88 and 90 we obtain the most stable isotopes with masses of 247 and 249. The main isotopes of element no. 98 can be obtained by adding to the atomic weight of Dy (162.48) the numbers 88 and 90. In this case the main isotopes of element no. 98 will be 250, 251, and 252. These values for the main isotopes of elements Bk and Cf are in good agreement with the data of A. P. Znoiko [13] and I. Selinov [14] which were derived from other theoretical considerations.

We now turn to the third type of nuclear periodicity.

Some considerable time ago the work of Aston indicated the presence of some similarities in the percent abundance of isotopes and in the value of the differences of 44 and 48 which were clearly manifested in the groups of magnesium, zinc, cadmium, etc. In Aston's opinion, however, "...all the relationships may be purely fortuitous" [11] and not linked together.

It can be demonstrated that the percent abundance of isotopes in the pleiads is subject to the laws of nuclear periodicity.

In fact, from the periodicity of the even and odd elements and the existence of pleiad-twins there follows the first law of distribution of isotopes of greatest percent abundance which may be formulated thus: in an unbroken series of isotopes the isotopes of greatest percent abundance of even and odd elements are arranged in pairs with a mass difference of only one unit, for example, $_{11}B$ - $_{12}C$, $_{23}Na$ - $_{24}Mg$, etc. The exception is represented by twin element pairs which are rendered more complex, in Shchukarev's phrase, by isobaric debris.

From the second form of nuclear periodicity of the Mendeleev type there is derived the similarity in percent distribution along the simple groups. To the

data put forward by Aston can now be added a whole series of data confirming this dependence: the similarity in percent distribution of the isotopes of carbon and silicon, ruthenium and osmium, barium and mercury, krypton and xenon, etc. Incidentally we may note that the differences of 44 and 48 noted by Aston enter into the nodal points of the system of pleiads of isotopes.

The two laws enunciated above concerning the distribution of isotopes of greatest percent abundance are distorted by the third form of nuclear periodicity which is manifested when the main isotope is shifted to the end of the pleiad. From the commencement of the system up to gallium the isotopes of greatest percent abundance in the pleiads of isotopes of even elements follow after the main isotopes of odd elements. The exceptions comprise the six pairs which are complexed by isobaric debris. The element gallium serves as a boundary line at which the order of distribution of the isotopes of highest percent content changes. Starting from germanium, the isotopes of greatest percent abundance of the even elements precede the isotopes of greatest percent abundance of odd elements in passage to the right towards, or at the end of, the pleiads. This leads to intersection of the perissad and artiad curves in Shchukarev's system of isotopes, and subsequently causes the perissad curve to pass below the artiad curve; it also gives rise to a series of other regularities which he observed. This circumstance actually makes clear to us a point which puzzled Aston, namely why in the zinc group the light isotopes are the most abundant, while in the barium group the opposite is the case. Displacement of the main isotopes in the pleiads is bound up with a change in the specific charge of the nuclei, a fact which enabled A. P. Znoiko [15] to represent this form of periodicity in the form of special nuclear periods and to observe the existence of the main isotope-analogs of the elements, which we had predicted from the existence of nuclear periodicity of the Mendeleev type.

It should also be mentioned that very frequently the displacement of the main isotope to the end of the pleiad is associated with a decrease in the abundance of the element in nature. This applies not only to the majority of elements following gallium, but also to the series of elements in the top part of the periodic system. Among these elements are lithium, beryllium and boron. Conversely, the presence of an isotope of greatest percent abundance at the commencement of a pleiad leads to an increased abundance even in the case of odd elements such as hydrogen, nitrogen and chlorine.

In the region of radioactive elements the role of isotopes of greatest percent abundance is played by isotopes with the longest life period with all the regular features inherent in them.

The data on the isotopic composition of the elements used in this paper are taken from the tables of S. Petrovich [16].

SUMMARY

1. A system of the pleiads of the natural isotopes is proposed which clearly expresses a nuclear periodicity of the Mendeleev type and correlates the chemical and nuclear properties of the elements; the guiding factor in the construction of the system was the philosophic pronouncement of I. V. Stalin in conjunction with the principles applied by D. I. Mendeleev in the creation of the general periodic system.

2. The system of pleiads of isotopes constitutes a generalization of a large number of data on the periodic properties of nuclei accumulated by science over a period of nearly 100 years, starting from the difference between the periods in atomic units and finishing with the empirical laws of recent years on isotopic abundance. At the same time it reflects the complexity of nuclear periodicity as described in the studies of Shchukarev and other investigators.

3. The proposed system of isotopes contributes to our knowledge of the twin elements, clarifies the laws of distribution of isotopes of greatest percent abundance, predicts the discovery of some heavy isotopes, and brings forward a whole series of questions for further investigation.

4. The study has a certain significance for the philosophical understanding of the periodic system, eliminating the metaphysical approach to the study of the chemical and nuclear properties of elements, establishing the unity of the periodic properties of the atomic nucleus and its electronic shells.

In its new treatment the periodic system links the properties of atoms with their construction from identical units, crystallizes our concepts of the transition from quantity to quality, and leads smoothly to an understanding of the periodic law from the standpoint of the basic law of dialectics -- the law of unity and the conflict of opposites.

The little-marked difference between the chemical properties of isotopes of the same element permits the complete series of them to be represented in the form of the separate symbols of the elements in tables of the normal type, although the pleiads of isotopes are genetically linked together to form a continuous chain of atoms in which the properties vary as a result of quantitative deviations and pronounced jumps. From the statistical system of the elements, we pass to the dynamic system of atoms in which natural and artificial radioactivity reflects the change of the periodic system with passage of time.

5. In the interpretation of the periodic law and system by D. I. Mendeleev there were, in essence, linked together the properties of the atomic nucleus of the element and the periodic properties of its external electronic structures which determine the chemical properties of elements. Nobody before D. I. Mendeleev or after him had considered so universally the interdependence of the elements, for the later development of science was bound up for a long time with one aspect of the periodic system -- the clarification of the periodic properties of elements as a function of electronic structures and of the quantum states of electrons in the outer shells.

In the light of the ideas enunciated by S. A. Shchukarev and ourselves, the scientific achievement of D. I. Mendeleev is illuminated from a fresh angle: In the regular change of atomic weights of the elements (the relation between twin elements, the existence of two types of twins, the regular change in the magnitude of the difference in atomic weights of element-analogs) he detected some aspects of nuclear periodicity, on the basis of which we may conclude that D. I. Mendeleev is also entitled to priority in the discovery of certain features of nuclear periodicity. He could not, of course, have been actually aware of this concept.

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REDUCTION OF SILICOTUNGSTATES BY HYDROGEN

IV. SODIUM BRONZE AND THE REDUCTION OF SODIUM SILICOTUNGSTATE

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Sodium bronze was first prepared by Wohler in 1824 on reducing sodium paratungstate with hydrogen. The author prepared gold bronze containing WO_3 92.4% and Na_2O 10 to 6% [1].

Malaguti [2] repeated Wohler's experiments and obtained gold bronze for which he proposed the formula $Na_2W_3O_9$. His analyses gave WO_3 93.15% and Na_2O 8.06%. Later investigations of the reduction of polytungstates by solid reducing agents showed that bronzes were similarly obtained by heating with phosphorus, zinc and tin. Of these the best results were obtained with tin metal. On reducing polytungstates by this method, Wright [3] obtained gold bronze with a WO_3 content of 93.55% and 93.61% and a specific gravity of 6.617. Wright [3] pointed out that the bronzes were full conductors. He also established that depending upon the temperature and duration of reduction of the polytungstate there are obtained, apart from gold bronze, reddish-yellow, purple-red and blue bronzes. In Philipp's paper [4], which described a repetition of the preparation of all the bronzes described by Wright, the following composition is given for gold bronze: Na_2O 10.88 to 10.19%, WO_3 91.71 to 92.50%. Philipp's analyses agree well with those of Wohler. Philipp proposed the formulas $Na_2W_2O_8$ and $Na_5W_8O_{18}$ for gold bronze. On electrolyzing fused paratungstate Scheibler [5] obtained a blue bronze with a specific gravity of 7.283. Hallopeau [6] prepared a blue sodium bronze on brief reduction of sodium paratungstate with tin. More prolonged reduction gave him a mixture of golden and blue bronzes.

An extremely thorough investigation of bronzes was undertaken by Spitsyn [7]. He studied the temperature of formation of different sodium bronzes, the mechanism of transformation of various tungstates into bronzes, and also the reciprocal transformations of the different bronzes. V. I. Spitsyn showed that by careful reduction of blue bronze it is possible to prepare first violet and then red and yellow bronzes on passage to the interior of the tungstate. Further reduction by hydrogen leads to complete separation of metallic tungsten in accordance with the equation: $Na_2WO_4 + 3H_2 = W + 2NaOH + 2H_2O$. This reaction takes place quantitatively at 1100° and can be applied to analytical determination of tungsten in different bronzes. Transition from one bronze to the other proceeds gradually during the reduction process. The consequence of this, according to Spitsyn, is that it is impossible to accurately fix the temperature range of existence of one or the other bronze. The limiting temperatures of formation of bronzes may be considered to be 550-650°. At 650-700° the bronzes are reduced with formation of neutral sodium tungstate and metallic tungsten. Comparing his own experiments on the hydrochlorination of bronze and the results of Brunner [8], V. I. Spitsyn considers that the formula of gold bronze must be trebled. According to Werner [9] tungsten bronzes should be regarded as heteropoly compounds in which WO_3 is combined with Me_2WO_3.

De-Yong [10], investigating the sodium bronzes, observed that many of them are isolated as cubic crystals and are isotropic bodies in incident light;

he examined them by the X-ray powder method and found that they belong to the perovskite type with a length of cube edge of a = 3.83 Å. Structural analysis of gold bronze gave the formula $NaWO_3$ or $NaHWO_3$, which was entirely inconsistent with the formula based on chemical analysis ($Na_2W_2O_6$). De-Yong concluded that in red and violet bronzes the atoms of hydrogen partly displace sodium atoms. Attention should also be drawn to the work of Hagg on sodium bronzes [11]. He prepared bronzes by Brunner's method. Analysis of his gold bronze revealed a formula of Na_xWO_3, where x ranges from 0.93 to 0.32; however, not a single analytical value is given in Hagg's paper. X-ray examination by Hagg gave an edge length of the unit cube of gold bronze of 3.859 Å, and a density of 7.24; Like De-Yong, Hagg assumed a perorskite structure for bronzes. He associates the deepening of the color of bronzes with a valency change of the W^{+5} ion to W^{+6}, this being accompanied by a change in the number of sodium ions in the bronze. Hagg found that cubic sodium bronzes possess a very stable W--O lattice in the voids of which occur sodium ions in quantity varying with the valence of the tungsten. All bronzes belong to one phase and within the limits of existence of this phase the sodium ion concentration can vary continuously. Hagg considered it impossible to assign a specific formula to an individual preparation. Study of the electric conductivity of bronzes showed that in the temperature interval of 20 and 350° they are electronic semiconductors with a high electric conductivity and a low temperature dependency of the latter. Hagg regarded bronzes as implanted structures (solid solutions with a varying number of atoms in the unit cell of the lattice). In all cases where the number of atoms is variable the structure contains voluminous ions (in this case, for instance, oxygen ions). Ions which vary in number (in the present case Na^+) are always relatively small and are located in the interstices of the framework composed of the large ions. These small ions can vary in number if the lattice contains ions capable of varying in charge.

Anderson [12] believes that the methods of preparation and the properties of the latter are not reproducible and that the dimensions of the unit cell of the lattice vary continuously from blue bronze to gold bronze. Noting the structural similarity of bronzes to WO_3, Anderson points out that the reduction of WO_3 by atomic hydrogen gives a dark-violet substance to which the formula $W_4O_{10}(OH)_2$ may be ascribed. This substance decomposes when heated to form the oxide W_4O_{11} and a new substance with the composition $W_4O_{12}nH_2$ where n is less than unity. The latter compound can apparently be regarded as a hydrogen analog (acid) of tungsten bronzes, and hence we can regard bronzes as representatives of the heteropoly compounds. Glazunov and Jolkin [13] do not regard bronzes as individual compounds but as different modifications of one phase or a mixture of two or three chemical compounds. A. A. Kalandiya and O. E. Zvyagintsev [14] repeated the work of V. I. Spitsyn and entirely confirmed his observations. In addition the authors studied bronzes by the method of electric conductivity and thermal analysis. They suggest that bronzes have a chain-like structure. Van-Duyn [15] prepared a series of bronzes from a mixture of Na_2WO_4 and WO_3 under conditions of slow and careful reduction with hydrogen and a mixture of hydrogen and nitrogen containing water vapor. The resultant bronzes were subjected to X-ray and metallographic examination. The data showed that bronzes form a series of solid solutions of cubic structure with a cell dimension of 3.838 to 3.839 Å.

It is evident from the above survey that the nature of bronzes has not yet been fully clarified; this state of affairs is due to the great difficulty of preparing and analyzing them. They can be regarded as berthollides or as implanted structures and heteropoly compounds.

Preparation of sodium bronze. We prepared sodium bronze by reduction of sodium paratungstate with dry hydrogen under conditions similar to those for the

preparation of potassium bronze [16]. The initial sodium paratungstate had the composition: WO_3 80.04%, Na_2O 9.70%, H_2O 10.95%. The bronze obtained had the composition Na_2O 11.79%, W 72.85% (calculated for $Na_2W_2O_6$: Na_2O 12.32%, W 72.16%). X-ray analysis revealed a cubic lattice with parameters a = 3.87 Å (for calculation of the X-ray diagram see Table 2 in which are given $\sin^2\vartheta$ observed on the X-ray diagram and $\sin^2\vartheta$ theoretically calculated for a cubic lattice with parameters of a = 3.87 Å). The X-ray measurements were kindly made by M. A. Vladimirova. Like potassium bronze, sodium bronze underwent further reduction with hydrogen at temperatures of 700, 750 and 800°; the reduction products were analyzed for removable alkali. Analytical results are shown in Table 1.

Table 1

Reduction of Yellow Sodium Bronze by Hydrogen

No.	Calcination temp.	Chemical analysis	
		Total Alkali in form of Na_2O (%)	Removable alkali in form of Na_2O
1	Initial bronze	11.79	0.2
2	700°	11.79	3.06
3	750	11.79	9.75
4	800	11.79	10.95

The analysis shows that decomposition of bronze starts at 700°.

The prepared bronze served as a standard in studies of the behavior of sodium silicotungstate (s.t.) when reduced with hydrogen.

Reduction of sodium s.t. For the purpose of clarifying the behavior of sodium s.t. when reduced with hydrogen, a tetra-substituted salt of the composition $Na_4H_4[Si(W_2O_7)_6]\cdot xH_2O$ was prepared. The preparation was effected under the same conditions as for tetra-substituted potassium s.t.

Large cubic crystals of the salt were isolated on crystallization (Figure 2).[1]

The chemical analysis of the prepared salt is given in Table 3.

Table 2

Calculations of the X-ray Diagram of Gold Sodium Bronze

Line No.	Intensity	$\sin^2\vartheta$ observed	h,k,l	$\sin^2\vartheta$ calcd. for cubic lattice with parameters of a = 3.87 Å.
1	Strong	0.062	012	0.062
2	Weak	0.104	011	0.102
3	Strong	0.125	011	0.124
4	Medium	0.187	011	0.187
5	Weak	0.205	002	0.204
6	Strong	0.251	002	0.247
7	Very Strong	0.305	012	0.307
8	Strong	0.375	112	0.373
9	Weak	0.462	003	0.460

[1]) See Plate, page 2349

Table 2 (continued from Page 2157)

No. of line	Intensity	$\sin^2\theta$ observed	h,k,l	$\sin^2\theta$ calculated for cubic lattice with parameters of a = 3.87 Å.
10	Medium	0.500	022	0.497
11	Strong	0.560	003	0.559
12	Strong	0.620	013	0.622
13	Weak	0.661	023	0.663
14	Medium	0.718	123	0.716
15	Strong	0.746	222	0.748
16	Strong	0.808	023	0.808
17	Very strong	0.872	123	0.870

Table 3

Analysis of Sodium S.T.

	Found %	Calculated on the basis of pure anhydrous salt	Calculated for the formula $2Na_2O \cdot SiO_2 \cdot WO_3$
WO_3 . . .	86.94	93.87	93.80
SiO_2 . . .	1.85	2.01	2.02
Na_2O . . .	3.98	4.12	4.1
H_2O . . .	7.01	-	-
Cl' . . .	0.18	-	-

It is seen from Table 3 that the preparation consists of the tetrasubstituted sodium salt of s.t. acid. The prepared sodium s.t. was reduced in a hydrogen atmosphere. The reduced specimens were subjected to chemical and X-ray analysis and to microscopic examination. Results are shown in Table 4.

Table 4

Reduction of Tetra-substituted Sodium S.T.

Temp.	Na_2O (in %)		X-ray measurements	Observations under microscope
	Total	Removable by washing		
500°	4.12	3.70	X-ray diagram not clear; lines diffused.	Grey-blue powder with colorless, lustrous crystals.
600	4.12	1.88	Lines of bronzes of low intensity	Yellow-gold crystals of bronzes. No original salt detected
700	4.12	1.26	All the interference lines belong to bronzes	Brownish-grey powder with a large quantity of yellowish-gold crystals of sodium bronze
800	4.12	3.34	Strong reflection from tungstate and from an unknown component	Dark-grey homogeneous powder

Calculations of the X-ray diagrams (Figures 2,3,4,5,6) are presented in Tables 5, 6 and 7.

Discussion of results for reduction of silicotungstates. The preparation of potassium s.t. again confirmed the systematics of heteropoly acids proposed by Miolati and Rosenheim which combined accordingly the boundary saturated acids with paratungstates in a single series. Reduction of potassium s.t., starting from the twelfth series and terminating with potassium paratungstate, leads us to one and the same final product - violet potassium bronze; reduction of sodium s.t. leads to gold sodium bronze. Study of the reduction reactions of potassium s.t. again confirms the correctness of the theory of structure of heteropoly acids of Miolati and Rosenheim, for without a close structural similarity between the starting compounds it would have been difficult to obtain one and the same product by reaction of hydrogen with all these complex compounds.

Table 5

Calculation of X-ray Diagram Prepared from a Specimen of Tetra-substituted Sodium S.T. Reduced with Hydrogen at 600°

Line No.	Intensity	$\sin^2\vartheta$ observed	h,k,l	$\sin^2\vartheta$ calcd. for a = 3.85 Å	Line No.	Intensity	$\sin^2\vartheta$ observed	h,k,l	$\sin^2\vartheta$ calcd. for a = 3.85 Å
1	Strong	0.0416	001	0.0400	11	Strong	0.400	222	0.404
2	Strong	0.523	—	—	12	Diffuse	0.438	023	0.438
3	Very strong	0.800	011	0.0799	13	Diffuse	0.514	023	0.518
4	Medium	0.100	111	0.100	14	Very strong	0.555	123	0.559
5	Strong	0.159	002	0.159	15	Strong	0.677	014	0.678
6	Very strong	0.202	112	0.202	16	Strong	0.719	033	0.718
7	Strong	0.242	112	0.240	17	Strong	0.757	133	0.758
8	Weak	0.300	003	0.302	18	Very strong	0.798	024	0.799
9	Medium	0.321	022	0.3196	19	Very strong	0.836	124	0.839
10	Strong	0.360	003	0.359	20	Strong	0.875	233	0.879

Table 6

Calculation of X-ray Diagram Prepared from Specimen of Tetra-substituted Sodium S.T. Reduced with Hydrogen Cu radiation

Line No.	Intensity	$\sin^2\vartheta$ observed	h,k,l	$\sin^2\vartheta$ calcd for a = 3.85 A	Line No.	Intensity	$\sin^2\vartheta$ observed	h,k,l	$\sin^2\vartheta$ calcd. for a = 3.85 Å
1	Strong	0.042	001	0.0400	12	Medium	0.438	023	0.438
2	Strong	0.081	011	0.0799	13	Strong	0.476	222	0.472
3	Blurred	0.101	111	0.100	14	Strong	0.515	023	0.518
4	Strong	0.120	111	0.120	15	Very strong	0.557	123	0.559
5	Strong	0.159	002	0.159	16	Very strong	0.677	014	1.679
6	Very strong	0.202	012	0.202	17	Very strong	0.715	033	0.718
7	Very strong	0.239	112	0.239	18	Diffuse	0.757	133	0.758
8	Strongly diffuse	0.297	003	0.302	19	Strong	0.799	024	0.799
					20	Very strong	0.840	124	0.838
9	Strong	0.322	022	0.320	21	Diffuse	0.878	233	0.879
10	Very strong	0.356	003	0.359					
11	Strong	0.400	013	0.399					

Table 7

Calculation of the X-ray Diagram Prepared with a Specimen of Tetra-substituted Sodium S.T. Reduced with Hydrogen at 800°

Line No.	Intensity	$\sin^2\Theta$ observed	h,k,l	$\sin^2\Theta$ calcd. for a = 3.85 A	Line No.	Intensity	$\sin^2\Theta$ observed	h,k,l	$\sin^2\Theta$ calcd. for a = 3.85 A
1	Medium	0.0881	—	—	9	Very strong	0.504	—	—
2	Very strong	0.120	011	0.119	10	Very weak	0.535	—	—
3	Diffuse	0.194	—	—	11	Very weak	0.559	—	—
4	Strong	0.240	002	0.138	12	Very strong	0.594	013	0.594
5	Diffuse	0.287	—	—	13	Medium	0.670	—	—
6	Very strong	0.357	112	0.356	14	Medium	0.713	222	0.713
7	Weak	0.388	—	—	15	Very strong	0.828	123	0.832
8	Very strong	0.478	022	0.475	16	Medium	0.863	—	—

The preparation of bronzes by reduction of s.t. enables us for the first time to attempt an experimental appraisal of the problem of the structure of the inner sphere of heteropoly acids. According to the theory of Miolati-Rosenheim, the inner sphere of these compounds contains W_2O_7 radicals; according to Kepin the inner sphere contains W_3O_{10} radicals; according to Pfeiffer WO_3 radicals, and these surround the central atom and the six non-equivalent ions of oxygen [17]. The preparation of numerous potassium silicotungstates from the 12th to the 5th series shows that with increasing alkali content one radical of WO_3 at a time is systematically displaced from the inner sphere; such a process is best explained on the basis of Pfeiffer's theory that heteropoly compounds contain WO_3 radicals as inner-sphere substituents, and the formula of silicotungstic acid will be $H_8[Si\begin{pmatrix}(O'')\\(O')_4\end{pmatrix}_2(WO_3)_{12}]$. Reduction of s.t. by hydrogen leads to the formation of potassium bronze, i.e. to the same product as that formed by reducing paratungstates. In the paratungstate $Na_5H_5[H_2(WO_4)_6]$ the inner sphere is unstable; the reaction of WO_4'' is quickly developed in aqueous solutions. On the other hand the inner sphere of the heteropoly acids is very stable, and if their reduction leads to the formation of bronzes, then we may conclude that their inner sphere is distinguished only by a greater stability, while the composition of the inner-sphere substituents is the same as in the paratungstates; consequently the possibility which we have demonstrated of the formation of s.t. salts and the study of the process of their reduction justify us in considering the structural formula of Pfeiffer to be the best founded. In the theory of Pfeiffer, however, the concept of the non-equivalence of the oxygen atoms which coordinate the WO_3 groups remains undemonstrated; we have undertaken the investigation necessary for final confirmation of these formulas. In order not to introduce even a slight degree of confusion there are already enough conflicting theories of the structure of the heteropoly acids, we are utilizing the formulas of Rosenheim which are the most generally accepted, until the theory of Pfeiffer has been finally confirmed.

Should bronzes be included among the heteropoly compounds The previously cited theory of Werner, our demonstration of the close relationship between heteropoly compounds of all series and bronzes, Anderson's data for the existence of a hydrogen analog of bronzes, i.e. of the existence of heteropoly acids from which it would be feasible to derive bronzes as salts -- all this evidence constitutes a prime justification for adopting this view. It is true that final confirmation will necessitate fresh and detailed evidence, but such a standpoint may prove fruitful as a working hypothesis.

The problem of potassium bronze is much simpler than that of sodium bronze.

Violet potassium bronze is the sole product of reduction by hydrogen of potassium isopolytungstates and heteropolytungstates; the conditions for their preparation and their composition are fully reproducible according to the investigations of various authors. Sodium bronzes are more numerous; four bronzes are known. The analytical data characterizing their composition are less consistent, apparently due to the greater difficulties of preparing sodium bronzes in the pure state. The X-ray investigations of bronzes performed by Hagg, De-Yong, Van Duyn and others lead us to regard bronzes as berthollides comprising a continuous series of solid solutions with a structure of the "implanted" type. This standpoint does not conflict with the assumption that bronzes are heteropoly compounds, since as far back as 1933 Bernal [18] classed both heteropoly compounds and tungsten bronzes among the berthollides.

We have pointed out that X-ray analysis leads us to a different conception of bronzes than does chemical analysis, namely to the assumption of the presence of pentavalent tungsten in sodium bronzes, etc. In any evaluation of the structural analysis it would be reckless to draw any final conclusions about the structure of sodium and other bronzes solely on the basis of their X-ray examination. The lattice of bronzes is built up from atoms of W and O, elements with atomic numbers of 8 and 74; as we know, structural analysis under such conditions is inaccurate. The difficulties in the study of bronzes are enormous; hence there are no reasons for rejecting the X-ray analysis. However, both in the case of heteropoly acids and of bronzes, the X-ray data do not give a conclusive answer to the problem of the nature of these complex compounds. A final solution to the problem calls for new experiments on their preparation, careful analysis and physicochemical examination. It may be possible to demonstrate the separate existence of the various sodium bronzes and bronzes of other metals.

Reduction of free cis-s.t. acid up to 400° is associated with gradual loss of its water of constitution; our own results are in accord with those of Marignac who found that complete removal of water during heating in the air takes place at above 350° and is accompanied by decomposition of the complex compound. We have been the first to investigate the dehydration of potassium s.t.; our results have shown that potassium s.t. firmly retains water, since decomposition of the complex is observed above 400° even under conditions of energetic reduction with hydrogen. Experiments with salts of cis-silicotungstic acid show that a considerable amount of water is expelled at 300 and 400°, which provides further evidence for regarding this water as constitutional. Partial reduction of potassium s.t. is observed at 400°, as indicated by the color change of the salts, the white crystals partly acquiring a greyish tone. With increasing content of K_2O in the s.t. the decomposition temperature rises; thus the hepta-substituted potassium s.t. remains undecomposed even at 500°, and the octa-substituted salt behaves similarly. The first supposed solid solution, prepared by introducing 9 equivalents of alkali into silicotungstic acid, decomposes completely below 500°, and we observe the formation of bronze already at a slightly higher temperature; the second solid solution, obtained by introducing 10 equivalents of alkali, is still stable at 500°. The third solid solution does not decompose at 500°. In the region of the conjectured solid solutions there is no regular increase in stability of the compounds; this is possibly associated with the relatively small change in their content of K_2O. Sodium s.t. is more stable than potassium s.t., dehydration is completed at above 500°, and formation of bronze is noted only at 600°. Only gold bronze is encountered when sodium s.t. is reduced, and therefore in our investigation we have considered only this type of sodium bronze.

Consideration of the results of analysis for the alkali removable by washing in the products of reduction of silicotungstates suggests that at 500°, after complete dehydration of the salt, decomposition of the heteropoly anion takes place and rearrangement of the lattice commences with formation of bronzes. The most intensive formation of bronzes takes place at 600°. At 700° and higher the process of reduction goes further and is accompanied by decomposition of the bronzes, as evidenced by the abrupt rise in the content of removable alkali. This process is almost entirely completed at 800°. It is not without interest to note the behavior of silicon during the reduction process. As shown by the analytical data for the removable alkali, the silicon is present to a considerable extent in the form of a soluble compound, most probably K_2SiO_3 (or Na_2SiO_3), in which case the process of reduction of silicotungstate can be schematically represented by the equation $K_8[Si(W_2O_7)_6]+3H_2 = 3K_2W_4O_{12}+K_2SiO_3+3H_2O$.

SUMMARY

1. Gold sodium bronze has been prepared; X-ray examination shows that bronze has a cubic lattice with parameters of a = 3.87 A.

2. The reduction of bronze by hydrogen in the temperature range of 700 to 800° has been studied.

3. Tetra-substituted sodium s.t. has been prepared; its reduction with hydrogen has been studied for the first time; it was established that gold sodium bronze is a reduction product.

4. The preparation of saturated and unsaturated potassium s.t., the preparation of tetra-substituted sodium s.t., and the study of the process of reduction of these compounds with hydrogen constitute the first experimental material for the solution of the problem of the structure of the inner sphere of the heteropoly acids.

5. The structural concepts of Pfeiffer most probably apply to the inner sphere of the heteropoly acids; these assume the presence of inner-sphere substituents in the form of WO_3 radicals.

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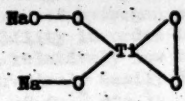
INVESTIGATION OF THE COLORED COMPLEX OF TITANIUM WITH HYDROGEN PEROXIDE

A. K. Babko and A. I. Volkova

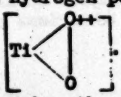
Hydrogen peroxide and its compounds with various metals have been repeatedly investigated by many workers. In the papers of I. A. Kazarnovsky [1], V. I. Kasatochnik [2] and others are discussed the general problems of the structure of hydrogen peroxide and some of its salts. Their data, however, are of value for the characterization mainly of the oxidizing properties of hydrogen peroxide, and give no information about the properties and conditions of formation of complex compounds of hydrogen peroxide with metals.

The classical studies of P. G. Melikov and L. V. Pisarzhevsky [3] contained extensive and valuable material concerning the properties of many peroxides and peracids, including the salts of pertitanic acid with peroxides of alkali metals. Nevertheless these researches of Melikov and Pisarzhevsky, like a series of other studies of the synthesis of many compounds of metals with hydrogen peroxide, fail to give information on the properties and conditions of formation of the complex groups themselves during reaction between the central ions (Ti, V, etc.) of complexes and hydrogen peroxide. For the further discussion it is important to note that the main objective of the researches of Melikov and Pisarzhevsky was the clarification of the problem: "Whether complex radicals -- residues of peroxides of metals of the type of MO or MO_2 -- play the part of simple metals in the formation of salts" [3].

These investigators represented the structure of, for instance, the sodium salt of pertitanic acid by the formula:



$+ 3H_2O$.

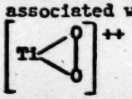
This formula, however, entirely fails to indicate that the actual complex portion of the compound of titanium with hydrogen peroxide under all conditions is the complex or  . As can be seen from the objective pursued by Melikov and Pisarzhevsky, the character of the bond and the composition of the complex group itself interested them less than the conditions of formation of the salts of peracids.

Furthermore, in connection with the problem of the preparation of the salts of pertitanic and other acids), all the syntheses in the investigations of Melikova and Pisarzhevsky were performed in such a manner that the components were reacted in an alkaline medium. Incidentally it is well-known from the practice of colorimetric determination of titanium that the intensely colored compound of titanium with hydrogen peroxide is formed in an acid medium, the color disappearing when the solution is made alkaline.[1] A series of other experiments show that various compounds, depending upon the acidity of the solution, are formed on reacting titanium with hydrogen peroxide, and these compounds differ not only in color but in many other properties. Thus, for

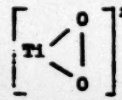
[1] Only in concentrated solutions does a very faint yellow color persist.

example, if oxalic acid (or another complex-forming agent) is added to a colored compound of titanium and hydrogen peroxide in an acid solution, the color is markedly weakened. For this reason we may conclude that the complex of titanium with oxalic acid is more stable than the colored complex of titanium with hydrogen peroxide. Moreover the addition of ammonia to the oxalic acid complex of titanium causes complete precipitation of titanium hydroxide, while the addition of ammonia to the solution of titanium and hydrogen peroxide only leads to decolorization of the solution and not to formation of a precipitate of titanium hydroxide. Consequently in an alkaline medium a complex of titanium with hydrogen peroxide is formed which differs profoundly from the complex formed in an acid medium in respect of the stability of the bond between the central and the coordinated ions.

More than theoretical interest is attached to the problem of the composition, character, stability and conditions of formation of the colored complex of titanium with hydrogen peroxide (in an acid medium). It is also important in connection with the practical application of such compounds in chemical analysis, in particular for colorimetric determination of titanium, vanadium and other elements, as well as for the determination of fluorine. It is generally assumed that the color is associated with the formation of the complex group



In the majority of cases, therefore, it is assumed that the colored complex is composed of a central Ti^{4+} ion (or of titanyl, TiO^{++}), while the coordinated group is an anion (O_2^{--}) of hydrogen peroxide. It is also known that hydrogen peroxide is a weak acid. According to the data of V. A. Kargin [4], which confirmed earlier data on the dissociation constant of hydrogen peroxide measured with the glass electrode, $K'_{H_2O_2} = 1.55 \cdot 10^{-12}$. Hence simple salts of hydrogen peroxide (not possessing a complex character) must be 50% hydrolyzed even at a pH of 11.8. Complexes of hydrogen peroxide should be characterized by extraordinarily high stability in order to remain stable towards acids. Experiment reveals, however, a relatively low stability of these complexes. It is known that they are comparatively easily decolorized on addition of other complex formers (ions of F^-, $C_2O_4^{--}$ etc.). Colorimetric determination of titanium, vanadium and a series of other elements is normally conducted in an acid medium; one effect of the acid is to split up these compounds when the coordinative ion O_2^{--}, forms part of the molecule of the weak acid H_2O_2:



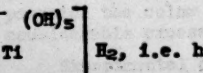
$$+ 2H^+ = Ti^{4+} + H_2O_2.$$

The widely held view that the color of the titanium[1] compound is formed as a result of substitution of the hydrogen atoms of hydrogen peroxide, i.e. the assumption that the coordinative group is the anion O_2^{--}, is inconsistent with a series of properties of these complexes as well as with the usual conditions for their application.

A few papers have appeared in the literature on the properties of the colored compounds of titanium with hydrogen peroxide in acid solutions. In the papers of F. Rivenq [6] and the thorough investigation of M. Rumpf [5], for instance, it was established that the colored compound is formed by interaction of one g-ion of titanium with one g-mole of hydrogen peroxide. Furthermore, Rumpf calculated the equilibrium constant for the formation of the colored

[1] Likewise of vanadium, etc.

complex. These papers likewise do not discuss the problem of the nature of the compound. Without carrying out any special experiments with the aim of clarifying the composition of the coordinative groups, M. Rumpf ascribes to the peroxy compound of vanadium the formula and to that of titanium the formula

 H_2, i.e. he assumes that in the formation of the vanadium complex the coordinative ions are O_2^{--}, while in the complex of titanium the coordinative ion of the acid salt is HO_2^-.

Physicochemical Analysis of the System Ti^{4+}—H_2O_2 (in Solution)

We applied the method of physicochemical analysis of complex compounds in solution [7] to the study of the composition and stability of the colored complex of titanium and hydrogen peroxide. The nature of the compound in relation to the effect of acidity is discussed separately below.

The composition of the system Ti^{4+}—H_2O_2 in solution can be presented by the triangle Ti^{4+}—H_2O_2—H_2O (Figure 1). The property selected for study was the optical density of the solutions. Measurement of the optical density was performed with a "ZH" photometer of the Pulfrich type, using a light filter with a transmittance zone of 465 mμ. For the determination of the composition and stability of the compounds the sections of the triangle parallel to its sides are the most important.

Section 1. Mixtures were prepared of equimolar solutions (10^{-3} molar) of titanium tetrachloride and hydrogen peroxide in various ratios at constant total volume of the mixture. Similar experiments were performed with titanium sulfate. The acidity of all the solutions was identical. Results of measurements of the optical density of this series of solutions are presented in Figure 2. In addition to the experiments with concentrations of 10^{-3} mole per liter, experiments were undertaken with 10^{-1} molar concentration. The optical densities of the second series were measured in thin cells with d = 0.05 mm.

In all cases the maximum absorption was observed at a 1:1 ratio of the volumes of the equimolar solutions.

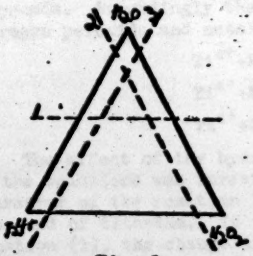


Fig. 1

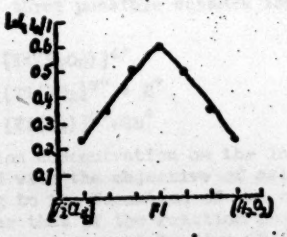


Fig. 2

These experiments accordingly confirm certain data of M. Rumpf and other investigators, and they also indicate that over a wide range of concentrations in acid solutions the color of the compound is due to interaction of one g-ion of titanium with one g-mole of hydrogen peroxide.

Section 2. In a series of solutions the titanium concentration was constant ($2 \cdot 10^{-3}$ molar), the concentration of the hydrogen peroxide varied from $0.9 \cdot 10^{-3}$ to $5.0 \cdot 10^{-2}$ molar. Results of measurements of the optical density are plotted in Figure 3. The curve does not possess a sharp inflexion point, pointing to a certain degree of dissociation of the complex. Inflexion is observed, however, in the vicinity of a 1:1 ratio of Ti to H_2O_2. With a slight excess of hydrogen peroxide the color becomes constant and does not change further in presence of a considerable excess of hydrogen peroxide.

Experimental data in the vicinity of the inflexion point of the curve were used for calculating the dissociation constant. These calculation (see below) likewise confirm that in the equation of the reaction: $aTi^{4+} + bH_2O_2 = Ti_a(H_2O_2)_b$, the coefficients a and b are equal, i.e. the colored compound is formed from one g-ion of titanium and one g-mole of hydrogen peroxide.

Section 3. In a series of experiments the hydrogen peroxide concentration was constant ($2 \cdot 10^{-3}$ molar), the titanium tetrachloride concentration was varied from $0.6 \cdot 10^{-3}$ to $3.0 \cdot 10^{-2}$ molar. Optical density measurements are plotted in Figure 4.

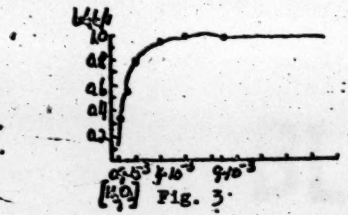


Fig. 3.

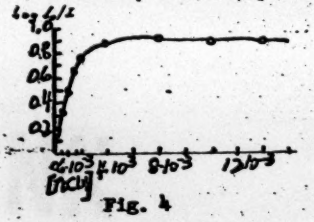


Fig. 4

This series of experiments likewise confirmed the conclusions drawn from a study of Section 2, and no new compounds whatever were observed.

Clarification of the Character of the Peroxy Compound of Titanium

The coordinating groups in complex compounds of metals with hydrogen peroxide may be anions of hydrogen peroxide (O_2^{--} and HO_2^-). The formation of such complexes depends to a great extent on the hydrogen ion concentration [8].

The coordinating groups could also be molecules of hydrogen peroxide, i.e. the product of reaction between metals and hydrogen peroxide might be addition compounds. Accordingly there are three possible schemes for the reaction between hydrogen peroxide and metals:

$$Ti^{4+} + H_2O_2 = [Ti(H_2O_2)]^{4+} \qquad (1)$$

$$Ti^{4+} + H_2O_2 = [Ti(HO_2]^{3+} + H^+ \qquad (2)$$

$$Ti^{4+} + H_2O_2 = [Ti(O_2)]^{2+} + 2H^+ \qquad (3)$$

The effect of the hydrogen ion concentration on the intensity of the color of the solutions was investigated with the objective of establishing the character of the reaction leading to the formation of the colored peroxy compound of titanium. It is clear that if the reaction proceeds according to equation (1), the change in hydrogen ion concentration should not influence the color of the solution. But if the coordinative ions are HO_2^- or O_2^{--}, then the color would be appreciably weakened with increasing acidity of solution.

In a series of solutions containing identical concentrations of the peroxy compound of titanium ($2.25 \cdot 10^{-3}$) the hydrogen ion concentration was varied from pH = 3 to pH = 8, while in a second series it was varied from $[H^+] = 10^{-4}$ to $[H^+] = 7$ N. Table 1 contains the results of the first series. Thickness of solution layer d = 1 cm.

Table 1

No.	pH of buffer solution	log I_0/I	No.	pH of buffer solution	log I_0/I
1	2.98	0.65	4	5.92	0
2	3.95	0.15	5	7.03	0
3	4.92	0	6	7.91	0

It is seen from Table 1 that the colored peroxy compound is formed in an acid medium up to pH = 3, while with reduction in acidity to pH = 5 and higher, a colorless peroxy compound is formed (no precipitate of titanium hydroxide is formed during the process).

Results of the second series of experiments (at higher acidity) are shown in Table 2. Thickness of solution layer d = 1 cm. The concentration of the peroxy compound of titanium was $2.25 \cdot 10^{-3}$ g-mole/liter.

Table 2

No.	Hydrogen ion conc. (normality of solution)	log I_0/I	No.	Hydrogen ion conc. (normality of solution)	log I_0/I
1	1.10^{-4}	0.15	6	1.0	0.83
2	1.10^{-3}	0.65	7	3.0	0.83
3	0.1	0.82	8	5.0	0.83
4	0.3	0.83	9	6.0	0.83
5	0.6	0.83	10	7.0	0.78

If the colored peroxy compound of titanium had been formed according to reaction (2) or (3), then with increasing hydrogen ion concentration a weakening of the color of the peroxy compound of titanium would be expected due to bonding of the HO_2^- or O_2^{--} ions in the molecule of the weak acid.

The data of Table 2 show that a change in the hydrogen ion concentration in the range of $[H^+]$ = 0.3 N to $[H^+]$ = 6 N has no effect upon the intensity of the color of the peroxy compound of titanium.

This great stability of the complex towards changing hydrogen ion concentration may be due either to complex formation taking place only according to equation (1) or to the fact that compounds in which the coordinating ions are HO_2^- or O_2^{--} possess an extremely high degree of stability [equations (2) and (3)]. The second alternative, however, is not supported by other experiments. The absence of a sharp inflexion on the plots in Figures 2, 3 and 4, also the calculations of the constant (see below), quite definitely point to appreciable dissociation, i.e. low stability of the coordinative shell of the colored compound. The absence of an appreciable dependence on the hydrogen ion concentration is bound up with the fact that H^+ ions in an acid medium do not participate in the equilibrium (1), i.e. the coordinative group is a molecule of hydrogen peroxide. In order to obtain further confirmation of this conclusion we performed a series of experiments on the behavior of the colored compound during electrolysis.

It is seen from equation (1) that the charge on the products of addition of a molecule of hydrogen peroxide does not differ from the charge on titanium ions. Even if titanium is present in the form of the titanyl ion (TiO^{++}) or in other complex forms, the addition of a neutral molecule of hydrogen peroxide should not change the charge of this complex group. In the event of displacement by a molecule of hydrogen peroxide of any other negative ions from the coordination sphere the charge must become more positive. Again, if the coordinating ion is HO_2^- or O_2^{--}, then the formation of a colored complex will in the general case alter the charge on the simple or complex titanium ion, making it more negative.

A series of experiments was performed in which transfer was observed of titanium during electrolysis of solutions of various compositions. In agreement with literature data it was observed that in weakly acid solutions of titanium sulfate or chlorides, the titanium migrated towards the cathode, whereas with a high concentration of hydrochloric or sulfuric acid it migrated to the anode, apparently owing to the formation of complex ions of $TiCl_5^-$ or $TiCl_6^{--}$. Introduction of hydrogen peroxide into all the solutions led to the development of color; during electrolysis of these colored solutions the direction of movement of the colored layer remained the same as that of the movement of titanium in corresponding solutions free from hydrogen peroxide. Consequently the formation of the colored compound with hydrogen peroxide does not alter the charge on the simple or complex titanium ions. This phenomenon supports the conclusion that the yellow-colored compound is a product of addition to titanium of a molecule of hydrogen peroxide and not of HO_2^- or O_2^{--} ions.

Determination of the Composition of the Compound of Titanium with Hydrogen Peroxide in a Weakly Acid Medium

At the start of this paper it was noted that the color of solutions of titanium with hydrogen peroxide is markedly weakened when the acidity is reduced to pH >3. This is not associated, however, with the decomposition of the complex owing to the interaction of the neutral Ti^{4+} ion with the OH^- ion and precipitation of titanium hydroxide. No precipitate is formed when the pH of the solution is increased; the freshly precipitated titanium hydroxide dissolves on addition of hydrogen peroxide and ammonia. Increased pH is therefore accompanied by formation of a new stable complex compound free from color.

The following series of experiments were undertaken with a view of elucidating the composition of this compound.

a) Study of the system: titanium salicylate -- hydrogen peroxide. An orange-colored solution of titanium salicylate was prepared from titanium sulfate and a fourfold excess of salicylic acid. The excess of acid was then neutralized, and to the solution was added a buffer mixture in order to keep the pH of the solution equal to 5 (in the other series of experiments the pH = 6). This solution was mixed with an equimolar solution of hydrogen peroxide in various ratios while the sum of the volumes was kept constant. Under the given conditions (pH = 5 or 6) introduction of hydrogen peroxide leads to decolorization of the solution. Results of measurements and calculations are plotted in Figure 5. Curve 1 represents the optical density of the solutions prepared from titanium salicylate and hydrogen peroxide as described above. Curve 2 shows the optical density of a series of blank experiments with solutions in which the place of hydrogen peroxide solution was taken by a corresponding volume of water. Curve 3 characterizes the difference between curves 1 and 2. We see from curve 3 that the maximum of formation of the colorless complex is observed at a 1:1 ratio of Ti to H_2O_2.

b) Study of the equilibrium constant of the reaction. The data for the composition of the colorless complex were confirmed by an investigation of the equilibrium constant of the reaction between the colored titanium salicylate complex and hydrogen peroxide.

In a series of experiments calculations were made of the equilibrium constant of the reaction $TiSal_n + xH_2O_2 = Ti(H_2O_2)_x + nSal$ when $x = 1$, $x = 2$, $x = 3$ (x is a coefficient for hydrogen peroxide). It appeared that when $x = 1$ the equilibrium

constant remained constant for a series of experiments. Consequently the colorless compound of titanium with hydrogen peroxide is formed in weakly acid solution by interaction of one g-ion of titanium with one g-mole of hydrogen peroxide. In this respect the colorless complex is similar to the colored complex which is formed in an acid medium, i.e. both compounds -- the yellow complex and the colorless complex -- are products of reaction of one g-ion of titanium with one g-mole of hydrogen peroxide. In a strongly acid medium however, an addition product is formed, while at pH = 5 there is apparently formed a stable complex compound of titanium with the anion of hydrogen peroxide, i.e. under these latter conditions the coordinative group is not the hydrogen peroxide molecule but the HO_2^- ion or possibly the O_2^{--} ion.

Calculation of the Dissociation Constant of the Colored Titanium Complex (in a Strongly Acid Medium)

The following method was used in the determination and calculation of the dissociation constant of the colored titanium complex. A series of solutions was prepared with various contents of titanium tetrachloride and hydrogen peroxide. The concentration of the colored complex in these solutions was determined from the calibration curve plotted on the basis of measurements of the optical density of standard solutions. The concentration of free titanium ions and free hydrogen peroxide was determined from the difference between the initial concentrations of titanium ions (or hydrogen peroxide) and the concentration of the colored complex.

On the basis of these data the dissociation constant was calculated from the equation:

$$K_{[TiH_2O_2]} = \frac{[Ti^{4+}][H_2O_2]}{[Ti(H_2O_2)^{4+}]}.$$

Fig. 5

Experimental and calculated values are given in Table 3.

Table 3

No.	Conc. of $TiCl_4$ in the mixture	Conc. of H_2O_2 in the mixture	log I_0/I	Conc. of the colored complex	Conc. of free titanium ions	Conc. of free hydrogen peroxide	Dissociation constant (K)
1	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	0.38	$0.70 \cdot 10^{-3}$	$0.30 \cdot 10^{-3}$	$0.30 \cdot 10^{-3}$	$1.3 \cdot 10^{-4}$
2	$1.6 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	0.46	$0.90 \cdot 10^{-3}$	$0.70 \cdot 10^{-3}$	$0.1 \cdot 10^{-3}$	$0.8 \cdot 10^{-4}$
3	$2.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	0.73	$1.56 \cdot 10^{-3}$	$0.44 \cdot 10^{-3}$	$0.44 \cdot 10^{-3}$	$1.2 \cdot 10^{-4}$
4	$2.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	0.87	$1.88 \cdot 10^{-3}$	$0.12 \cdot 10^{-3}$	$1.12 \cdot 10^{-3}$	$0.7 \cdot 10^{-4}$
5	$1.6 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	0.63	$1.30 \cdot 10^{-3}$	$0.30 \cdot 10^{-3}$	$0.30 \cdot 10^{-3}$	$0.7 \cdot 10^{-4}$
6	$2.0 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	0.69	$1.44 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$0.16 \cdot 10^{-3}$	$0.6 \cdot 10^{-4}$

Mean value of K . . . . . $0.9 \cdot 10^{-4}$

SUMMARY

It was established that hydrogen peroxide forms two peroxy compounds with titanium: a colored peroxy compound formed in a strongly acidic medium in the range of $[H^+] = 0.3$ N to $[H^+] = 6$ N, and a colorless peroxy compound formed in a weakly acid medium at pH = 5 and higher. Both of the investigated peroxy compounds have the same ratio (1:1) of Ti to H_2O_2. On the basis of a study of the influence of the hydrogen ion concentration of the solution on the intensity of the color, and also of a study of the movement of the ions during electrolysis, it was established that the colored peroxy compound of titanium is an addition product, i.e. the coordinating group is the H_2O_2 molecule. The colorless peroxy compound formed at pH = 5 and higher contains the HO_2^- or the O_2^{--} ion as the coordinating group.

The dissociation constant of the colored peroxy compound of titanium was calculated and found to have the value $K = 0.9 \cdot 10^{-4}$.

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HEATS OF FORMATION OF THE DOUBLE SALTS

$Li_2SO_4 \cdot K_2SO_4$, $BaF_2 \cdot BaCl_2$, and $SrF \cdot SrCl_2$

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The experimental determination of the heats of formation of the salts mentioned in the title was undertaken by us in connection with a series of extensive investigations, under the direction of A. G. Bergman, of the fusibility of reciprocal systems, and it had the immediate purpose of obtaining data for calculation of the thermal effects of double decompositions involving these salts.

The heats of formation were found from the difference between the heat of solution of the double salts and of mixtures of the separate salts.

In the case of $Li_2SO_4 \cdot K_2SO_4$ we measured the heat of solution of this salt only in water; the heat of solution of the mixture at the corresponding concentration was calculated from literature data. At the concentrations which we employed, the heat of solution of the mixture differed so slightly from the sums of the heats of solution of the individual salts that the difference could be ignored [1], [2]. In the case of the two other double salts determinations were made of the heat of solution and of the heat of solution of mixtures of the components.

Measurements were performed in a calorimeter with an isothermal jacket. The calorimeter was a silver beaker equipped with a tightly fitting cover. Through the cover were inserted a Beckmann thermometer, a propeller stirrer, a nichrome heating resistance in a copper foil sheath covered with a thin layer of varnish, a test tube for rapid cooling of the solution, and a suspension device to which was attached inside the calorimetric liquid a small flask containing a weighed amount of the salt. At the appropriate instant the flask was crushed. The heat capacity of the calorimetric system was determined by the method of electrical heating. The work of the current was calculated with the aid of a potentiometric circuit (a low-resistance potentiometer from the "Etalon" Works) and a timing device.

The temperature of the calorimeter was determined with the aid of the telescope on the standard Beckmann thermometer. The temperature of the water in the jacket was-25 $\pm 0.02°$. Corrections were introduced for heat exchange by the Regnault-Pfaundler formula, for the projecting mercury column,the calibration and the fundamental interval (the three latter according to the VIMS standard). Precisely identical weighed amounts of salts and solvent were used for the measurement of the heat of solution of the double salt and the mixture of single salts, as well as of the salts used in the parallel experiments. Due to the identical weights the heat capacity of the system after solution of the mixtures clearly did not differ from the heat capacity after solution of the corresponding double salts; therefore we determined it in only one case.

We prepared all three double salts by fusion of the components in stoichiometric proportions (as shown by the fusibility curves of the corresponding binary systems, all three salts melt congruently [3], [4]; this was confirmed in investigations by the Fused Salts Laboratory of our institute).

The chlorides and sulfates used ("chemically pure" grade) were twice recrystallized. The fluorides were prepared from the carbonates. The carbonates were prepared from recrystallized chlorides and ammonium carbonate. The carbonates were then treated with hydrofluoric acid which had been twice distilled in a platinum apparatus.

Each of the double salts investigated by us consists of individual salts with sharply differing solubilities. This difference is smallest for $Li_2SO_4 \cdot K_2SO_4$. Even in this case, however, as evident from the work of Spielrein [5] on solubilities in the system Li_2SO_4—K_2SO_4—H_2O, at both of the invariant points of the boundary lines of solubility of this salt in the aqueous ternary system the concentration in moles per 100ml of saturated solution of lithium salt at 25° exceeds the concentration of the potassium salt; it follows from this that the binary salt now under consideration dissolves incongruently with formation of K_2SO_4. From the same data it is seen that at higher temperatures the solubility becomes congruent and thus makes possible the preparation of this salt from an aqueous solution containing both salts in equivalent proportions [6] - [8].

The weighed amount that we used (20g $Li_2SO_4 \cdot K_2SO_4$ per 500 g water) ensured complete and sufficiently rapid solution. Since Li_2SO_4 dissolves with evolution of heat (due to hydration), while K_2SO_4 dissolves with heat absorption, and since the absolute values of both effects are very similar, the sign of the thermal effect of solution of the binary salt is governed by its heat of formation from the individual salts, and the temperature change during a dissolution experiment is insignificant. An increased weight of sample, however, prolonged the experiment, and this leads (in the case of a negligibly small thermal effect) to impermissibly large (percentage) corrections.

There are no data for the solubility of the ternary aqueous systems in which the two other binary salts under investigation are formed.

Our experiments demonstrated that if $BaF_2 \cdot BaCl_2$ and the corresponding strontium system are decomposed by water, then the process is so slow that even if this decomposition were complete the employment of pure water as solvent would be unsuitable because the calorimetric experiment would extend over an unduly long period of time. When $AgNO_3$ is present in the solvent the decomposition takes place fairly quickly as shown by Bergman and Bukhalova by titration with $AgNO_3$ solution of weighed amounts of the double salts in water. In this case the decomposition of the double salts proceeds to completion and is accompanied by formation of a precipitate of AgCl. It is realized that the designation of $AgNO_3$ as a solvent in the present instance is purely arbitrary. The solubility of BaF_2 and SrF_2 in water at 25° is considerably lower than the solubility of AgF (a liter of saturated solution contains 1.614 g BaF_2 and 0.39 g SrF_2, whereas the solubility of AgF at 24° is equal to 178 g per 100 g water [9], and therefore double decomposition between barium and strontium fluorides and $AgNO_3$ does not take place. The greater part of the BaF_2 and SrF_2 remains in the solid phase.

For the purpose of determining the heats of formation of $BaF_2 \cdot BaCl_2$ and $SrF_2 \cdot SrCl_2$ we measured the heat of reaction of these salts and of mixtures of the corresponding individual salts with a solution containing a large excess of $AgNO_3$ over the amount required by the equation for the double decomposition.

A disadvantage of the use of $AgNO_3$ solution as a solvent is the heat developed by the friction of the stirrer which is considerably increased by the voluminous flocculent precipitate of AgCl. Only after a few experiments was it possible to establish a speed of rotation of the stirrer ensuring a sufficiently slow decomposition of the salt while not distorting the course of the temperature change after completion of the reaction and during measurement of the heat capacity.

The direct results of the measurements are presented in the table. Here $\Delta t°$ denotes the change of temperature in the dissolution experiments, C the heat

capacity of the system after dissolution, L the heat of solution of one g-mole of double salt or the equivalent amount of mixture in water or $AgNO_3$ solution. This value was calculated from the average change of temperature and the average heat capacity. The relative error of the value of the heat of solution was calculated as the sum of the relative errors of two successive values; the weighing error was considerably smaller and was not taken into account.

Heats of Solution

Dissolving salt	Solvent	$\Delta t°$	C (in cal)	L (in cal/mole)
20.00 g double salt $Li_2SO_4 \cdot K_2SO_4$	500 g water	0.268 0.269 0.269±0.23%	496.7 498.3 497.3 497.4 ± 0.17%	+1898 ±0.40%
Mixture of 7.329 g $BaCl_2$ and 6.171 g BaF_2	13.5 $AgNO_3$ in 500 g water	2.191 2.173 2.182±0.40%	580.1 577.1 578.6±0.26%	-35890±0.67%
13.5 g double salt $BaF_2 \cdot BaCl_2$	13.5 g $AgNO_3$ in 500 g water	1.266 1.252 1.259±0.53%	--	-2C710±0.79%
Mixture[1] of 5.567 g $SrCl_2$ and 4.433 g SrF_2	13.5 g $AgNO_3$ in 500 g water	2.841 2.814 2.827±0.50%	546.7 548.9 547.8±0.20%	-44100±0.70%
10.00 g double salt $SrF_2 \cdot SrCl_2$	13.5 g $AgNO_3$ in 500 g water	2.109 2.120 2.114±0.24%	--	-32970±0.44%

[1] The weighed sample contains an excess of 0.022 g SrF_2 over the equivalent ratio; the same in the double salt. This obviously does not influence the result.

The thermodynamic law of signs is assumed to apply.

We give below a calculation of the thermal effect of the addition reactions of salts and of the heats of formation of the double salts from the elements. We use data from the handbook of Bichowsky and Rossini [10] for the heat of solution of Li_2SO_4 at the concentration encountered in our investigation, and for the heats of formation of all six single salts; the values of Mishchenko and Pronina [11] are taken for the heat of solution of K_2SO_4. We do not introduce corrections for the difference in temperatures prevailing in our experiments owing to their insignificance:

$$Li_2SO_4 + K_2SO_4 + nH_2O = Li_2SO_4 \cdot K_2SO_4 \cdot nH_2O \text{ solvent} \quad -- \quad 6233 + 5905 =$$

$$= Li_2SO_4 \cdot K_2SO_4 nH_2O \text{ solvent} \quad -328 \text{ cal};$$

$$Li_2SO_4 + K_2SO_4 = Li_2SO_4 \cdot K_2SO_4 \quad + \Delta H;$$

$$Li_2SO_4 \cdot K_2SO_4 + nH_2O = Li_2SO_4 \cdot K_2SO_4 \cdot nH_2O \text{ solvent} + 1898 \pm 7 \text{ cal}.$$

$\Delta H = -328 - 1898 = 2226 \pm 14$ cal (on the assumption that the calculated heat of solution of the mixture has the same error as our measured heats of solution of the double salt).

The heat of formation of the double salt $Li_2SO_4 \cdot K_2SO_4$ from the elements:

$$342.35+342.66+2.23 = 697.2 \text{ kcal}.$$

Interaction of a mixture of BaF_2 and $BaCl_2$ and of the corresponding double salt with $AgNO_3$ solution can be expressed by the equations:

$$BaF_2+BaCl_2+ AgNO_3 \text{ solution} = BaF_2+Ba(NO_3)_2 \text{ solution} + 2AgCl - 35890 \pm 240 \text{ cal.}$$

$$BaF_2+BaCl_2 = BaF_2 \cdot BaCl_2 + \Delta H;$$

$$BaF_2 \cdot BaCl_2 + AgNO_3 \text{ solution} = BaF_2+2Ba(NO_3)_2 \text{ solution} + 2AgCl - 20710 \pm 404 \text{ cal.}$$

$$\Delta H = -35890 - (-20710) = -15180 \pm 644 \text{ cal.}$$

The heat of formation of $BaF_2 \cdot BaCl_2$ from the elements:

$$283.9+205.28+15.2 = 508.4 \text{ kcal}.$$

From the equations for the reactions of a mixture of SrF_2 and $SrCl_2$ and of the double salt with $AgNO_3$ solution we find:

$$\Delta H = -44100 - (-32970) = -11130 \pm 454 \text{ cal.}$$

The heat of formation of $SrF_2 \cdot SrCl_2$ from the elements amounts to:

$$289.0+197.87+11.1 = 498.0 \text{ kcal}.$$

Since it has previously been shown [8] that crystals of $Li_2SO_4 \cdot K_2SO_4$ are altered by heat (its double refraction on heating from 0 to 420° increased 5 times, and at 435° the salt undergoes a polymorphic transformation [3, 8]), we carried out prolonged annealing--in the course of several days--of the salt at 300°, in order to avoid the presence in our solution experiments of phases which would reach equilibrium. The heat of solution of this annealed specimen did not differ from that given in the table and relating to freshly prepared (by fusion) salt. Since previous investigators had prepared $Li_2SO_4 \cdot K_2SO_4$ from aqueous solutions, a determination was made by our co-worker M. N. Lyashenko of the refractive index of specimens, annealed and non-annealed, prepared by fusion. The optical constants were in agreement, within the limits of measuring error, with the literature values. Consequently the salt obtained by fusion and without annealing is identical with that formed at room temperature from aqueous solution.

The thermal effect of the addition reaction of Li_2SO_4 with K_2SO_4 is similar to that of many other such reactions which lead to the formation of typical double salts — anhydrous and hydrated carnallite $KCl \cdot MgCl_2$ (-3.0 kcal.), $KCl \cdot MgCl_2 \cdot 6H_2O$ (-3.2 [12]), syngenite $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ (-2.016 kcal.), and other double sulfates of the alkali (Na, K, NH_4) and alkaline earth metals (Ca,Sr), likewise of Pb, obtained from aqueous solutions and examined for their heats of formation by Barre [13].

The salts $BaF_2 \cdot BaCl_2$ and $SrF_2 \cdot SrCl_2$ have lower heats of formation from the individual salts than those containing fluorides of Al: $3NaF \cdot AlF_3$ (21 kcal.), $3KF \cdot AlF_3$ (45 kcal.) [14], forming the complex anion AlF_6''', which is strongly dissociated in water [15].

The difference in character between Ba(Sr) ions and the Al ion does not justify any conclusions about the formation of complex ions from a comparison of the heats of formation of the double salts from one metal or the other. By analogy with PbFCl, a similar structure might be postulated for salts of Ba and Sr [16], but it is realized that this analogy cannot be pushed very far if we take

into account the different characters of Ba (Sr) and Pb ions. Judging by the high heat of formation of the double salts of Ba and Sr which we have investigated, their structure differs markedly from that attributed by Seifert [17] to salts containing two different anions for example, $Mg_2SiO_4 \cdot Mg(OH, F)_2$, $PbCl_2 \cdot PbCO_3$. Seifert regarded such salts as "molecular regular intergrowths" in which each of the component salts possesses its own layer. It might be expected that the heat of formation from the individual salts of such "molecular intergrowths" would be much smaller than for the above-mentioned double salts -- chlorides, sulfates and salts of the type of PbFCl -- since each salt retains its lattice with comparatively little modification. In the absence of data for the heats of formation of PbFCl and salts of the molecular intergrowth type, it is impossible at present to verify the correctness of this hypothesis.

SUMMARY

1. Experimental determinations have been made of the heats of interaction of salts leading to formation of the double salts named in the title.

2. The heats of formation of these double salts from the elements were calculated.

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THE SOLUBILITY PRODUCT OF HYDROXIDES

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When calculating the solubility product of difficulty soluble electrolytes the assumption is made that they are completely ionized in their saturated aqueous solutions. It is then easy to calculate the ionic concentration in the saturated solution and to find the ionic product. Such an assumption is valid for solutions of difficultly soluble salts, the majority of which are strong electrolytes, and the attainment of complete ionization is in full accord with the theory of electrolytic dissociation as well as with the theory of strong electrolytes. These considerations also apply to difficultly soluble weak electrolytes (for example, hydroxides of heavy metals) on the assumption that, due to the low concentration of their saturated solutions, such electrolytes here exist in a state of complete ionization. Such an assumption, however, leads to errors which prove to be more serious the weaker the electrolyte is. For correct calculation of the solubility product we must take into consideration the degree of ionization of the difficultly soluble electrolyte in its saturated solution, which is by no means always close to 100%.

We shall first consider the solubility product of AgOH. The solubility of this electrolyte is equal to 1.2×10^{-4} mole/l [1], and the ionization constant is 1.1×10^{-4} [2]. Assuming complete ionization of AgOH, the concentration of $Ag^{\cdot}$ and OH' ions is equivalent to the molar concentration of this electrolyte in saturated solution, i.e. 1.2×10^{-4} g-ion $Ag^{\cdot}$ or OH' in 1 liter of solution, so that the solubility product will be $(1.2 \times 10^{-4})^2 = 1.44 \times 10^{-8}$. This value, or one of similar order, enters into all reference tables. It can be shown that there is no justification for the assumption of complete ionization of AgOH in its saturated solution. We calculate the degree of ionization of AgOH in such a solution according to the dilution law:

$$\frac{\alpha^2 \cdot 1.2 \cdot 10^{-4}}{1 - \alpha} = 1.1 \cdot 10^{-4}. \quad \text{Hence } \alpha = 0.603 \text{ or } 60.3\%.$$

Consequently $[Ag^{\cdot}] = [OH'] = 1.2 \cdot 10^{-4} \cdot 0.603 = 7.24 \cdot 10^{-5}$ g-ion/l.

Hence the solubility product is equal to $(7.24 \cdot 10^{-5})^2 = 5.2 \cdot 10^{-9}$.

This value is three times smaller than the values from approximate calculation.

A more marked discrepancy between the approximate and the precise calculation is observed in the case of weaker electrolytes such as hydroxides of the type of $Me(OH)_2$. As an example we shall consider the calculation of the solubility product of $Pb(OH)_2$. The solubility of this hydroxide is 5.5×10^{-5} mole/l [1]. On the assumption of complete ionization we find that the value of $[Pb^{\cdot\cdot}]$ in a saturated solution of $Pb(OH)_2$ is equal to 5.5×10^{-5} g-ion/l, while that of $[OH']$ is twice as large, i.e. 1.1×10^{-4} g-ion/l. Hence the solubility product of $Pb(OH)_2$ is equal to $(5.5 \times 10^{-5}) \cdot (1.1 \cdot 10^{-4})^2 = 6.6 \cdot 10^{-13}$. However, the assumption of complete ionization can hardly be true for we know that $Pb(OH)_2$ is a weak electrolyte; its ionization constants as bases are [2]:

$$K' = 9.6 \cdot 10^{-4} \qquad K'' = 3 \cdot 10^{-8}.$$

The value of these constants enable us to establish the degree of ionization of this electrolyte and to more accurately calculate the concentration of ions in its saturated solution.

The first stage in the ionization is $Pb(OH)_2 \rightleftharpoons PbOH^{+} + OH'$, for which

$\frac{[PbOH^{\cdot}][OH']}{[Pb(OH)_2]} = 9.6 \cdot 10^{-4}$. In accordance with the dilution law:

$$\frac{\alpha^2 \cdot 5.5 \cdot 10^{-5}}{1-\alpha} = 9.6 \cdot 10^{-4}$$

Hence $\alpha = 0.9485$, or 94.85%. Therefore $[PbOH^{\cdot}] = [OH'] = 5.5 \times 10^{-5} \times 0.9485 = 5.217 \times 10^{-5}$ g-ion/per liter, while $[Pb(OH)_2] = 5.5 \cdot 10^{-5} - 5.217 \cdot 10^{-5} = 2.83 \cdot 10^{-6}$ mole/per liter. The second ionization stage is $PbOH^{\cdot} \rightleftarrows Pb^{\cdot\cdot} + OH'$, for which $\frac{[Pb^{\cdot\cdot}] \cdot [OH']}{[PbOH^{\cdot}]} = 3 \cdot 10^{-8}$.

The second ionization stage slightly reduces the concentration of $PbOH^{\cdot}$ ions and increases that of OH' ions, but these changes are insignificant due to the small magnitude of K", and therefore the above-stated equivalence of the concentrations of $PbOH^{\cdot}$ and OH' ions is maintained in practice. This has the effect of reducing these values in the last formula, giving $[Pb^{\cdot\cdot}] = 3 \cdot 10^{-8}$ g-ion/per liter. Substantially the same value is reached by a more accurate calculation of $[Pb^{\cdot\cdot}]$ according to the equation:

$$\frac{[Pb^{\cdot\cdot}](5.217 \cdot 10^{-5} + [Pb^{\cdot\cdot}])}{(5.217 \cdot 10^{-5} - [Pb^{\cdot\cdot}])} = 3 \cdot 10^{-8}.$$

Hence the solubility product of $Pb(OH)_2$ is equal to $3 \cdot 10^{-8} (5.217 \cdot 10^{-5})^2 = 8.17 \cdot 10^{-17}$. This value is 8000 times smaller than the values from approximate calculation.

According to literature data [4], $Pb(OH)_2$ begins to precipitate from a 0.02 M solution of $Pb(NO_3)_2$ at a pH of about 6. From this it follows that the solubility product of $Pb(OH)_2$ is:

$$\frac{0.02 \cdot (10^{-14})^2}{(10^{-6})^2} = 2 \cdot 10^{-18}$$ i.e., we obtain a value of the same order as that which we calculated on the basis of the solubility of $Pb(OH)_2$ when allowing for both of the ionization constants.

Similar calculations can be performed for those hydroxides the ionization constants of which are known. For HgO or $Hg(OH)_2$ the precise calculation of the solubility product leads to a magnitude of $3.1 \cdot 10^{-47}$ instead of the approximate value of $1.35 \cdot 10^{-26}$ given in the handbooks. Still greater deviations are bound to be observed with hydroxides of the type of $Me(OH)_3$. Unfortunately the absence of data for the ionization constants of such hydroxides prevents us from carrying out a direct accurate calculation of the solubility product from the value for the solubility. The assumption of complete ionization of these compounds in their saturated solutions is unfounded, and the values calculated on this basis for the solubility product, which can be found in all textbooks and handbooks, are far from accurate. For example, the solubility product of $Al(OH)_3$, calculated on the assumption of its complete ionization, is equal to $1.1 \cdot 10^{-15} - 4.7 \cdot 10^{-18}$ [1, 3], whereas the very same magnitude calculated on the basis of the pH of the solution at the start of precipitation of $Al(OH)_3$ is equal to about 10^{-32}.

SUMMARY

1. The solubility product of difficultly soluble hydroxides cannot be accurately calculated from the value of their solubility and on the assumption of complete ionization.

2. It is necessary to take also into consideration the ionization constant when calculating the solubility product of difficultly soluble hydroxides on the basis of their solubility.

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THE ACIDIC PROPERTIES OF MnO_4^-

M. Usanovich

The principal objection raised by Shatenshtein [2] and other authors to the concepts of acids and bases which I have developed [1] is that I erroneously regard oxidation-reduction processes as a special case of acid-base interaction. In an earlier review Luder [3], in particular, had regarded such an approach to oxidation-reduction processes as the main defect of my theory. In a recent publication Luder and Zuffanti [4] generally favor my theory, pointing out that the acid-base theory of Lewis in its original formulation did not exclude oxidation-reduction processes, but that they had attempted to broaden Lewis' theory by including oxidation-reduction processes in it. A similar development of my ideas is found in a paper by Charlot, Wolff and Lacroix [5]. In spite of this, however, Luder and Zuffanti persist in their criticism, asserting that although a close relationship exists between acid-base and oxidation-reduction processes, the relationship " is not of the type put forward by Usanovich" [6]. As a specific example these authors adduce the behavior of MnO_4^-: "for example, the permanganate ion is a strong oxidizing agent but not an acid".

I should now like to consider this example since it can be demonstrated with particular clarity in this case that no sharp division can be drawn between acid-base and oxidation-reduction processes.

It can be seen from the over-all equation for the transformation of potassium permanganate into manganate [7] that this oxidation-reduction process is at the very same time an acid-base interaction:

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + O.$$

The oxidation-reduction process is accompanied by the disappearance from the solution of the caustic alkali.

The modern stoichiometric equation of this reaction [8] takes the form:

$$4MnO_4^- + 2H_2O \longrightarrow 4MnO_4^{--} + O_2 + 4H^+.$$

We see from this equation that the oxidation-reduction process is accompanied by acidification.

It may be thought that the oxidation-reduction process and the acid-base interaction are separate stages in the reaction. In reality this is not so. Duke [8] recently investigated this reaction and reached the conclusion that the first stage is the following equilibrium:

$$MnO_4^- + H_2O \rightleftharpoons MnO_4^{--} + OH + H^+.$$

The MnO_4^- functions simultaneously as an oxidizing agent, converting water into free hydroxyl, and, as an acid, increasing the hydrogen ion concentration.

Therefore Luder and Zuffanti are in error when they assert that the permanganate ion is an oxidizing agent but not an acid. We see that the permanganate ion is capable of exhibiting oxidizing and acidic properties simultaneously.

SUMMARY

It is shown that the permanganate ion while functioning as an oxidizing agent behaves simultaneously like an acid.

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COMPLEX COMPOUNDS OF SOME BIVALENT METALS WITH ANTIPYRINE

V. I. Kutov

Antipyrine $CH_3N\begin{matrix}(2)\\ \\ CH_3C(3)\end{matrix}\begin{matrix}(1)NC_6H_5\\ (5)\\ =(4)CH\end{matrix}CO$ forms colorless leaflets and has a bitterish taste. It melts at 113° and is a monovalent base. Its aqueous solutions have a neutral reaction; with $FeCl_3$ the solutions turn red, and with nitrous acid they are green.

Ryabchikov established that antipyrine fairly easily forms a complex in which it occupies a single coordinate position. If we take Knopp's formula as a basis, then the only atom that can be coordinated with the central atom is the second, i.e. tertiary, atom which is attached to the methyl group. In 1945 Ryabchikov and Terenteva [1] succeeded in preparing a series of complex compounds of antipyrine with trivalent rare-earth metals with the general formulas $[Me(C_{11}H_{12}ON_2)_6]X_3$ and $[Me(C_{13}H_{17}ON_3)_6]X_3$, where Me = La, Ce, Pr, etc., and X = Cl', NO_3, ClO_4.

The investigations of Gusev and others [2, 3] showed that antipyrine $C_{11}H_{12}ON_2$ and pyramidone $C_{13}H_{17}ON_3$ can react in acid solution with a series of salts of bivalent metals, in consequence of which the following new complex compounds were synthesized:

$$[C_{11}H_{12}ON_2H]_2^{++}[MeX_4]^{--} \text{ and } [C_{13}H_{17}ON_3H]_2^{++}[MeX_4]^{--} \text{ where Me} = Zn^{2+}, Cd^{2+}, Pd^{2+}, \text{ and X} = CNS', I', Br', CN'.$$

Later investigations in our laboratory [4] showed that in neutral solution some pyramidone complexes can be obtained by direct reaction of salts of the corresponding metals with aqueous solutions of pyramidone. In this manner the synthesis was effected of a whole series of complex compounds with the general formula $[Me(C_{13}H_{17}ON_3)_2]X_2$ and $[Me(C_{13}H_{17}ON_3)]X_2$, where Me = Zn^{2+}, Cd^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, and X = CNS', Cl', Br' I'.

In the present paper the syntheses are described of some antipyrine complexes with bivalent metals. It was found that in presence of a bivalent metal the entry into the inner sphere of two molecules of antipyrine may take place in a neutral medium if certain conditions are maintained. The reaction in neutral solution between a salt of a bivalent metal and antipyrine can be expressed by the equation:

$$MeX_2 + 2Ant = [Me(Ant)_2]X_2, \qquad (1)$$

where Ant = $C_{11}H_{12}ON_2$ and X = Cl', Br', I', CNS'.

It is more difficult and sometimes even impossible to obtain the respective complex compounds by direct interchange of one anion by another in the outer sphere according to the equation:

$$[Me(Ant)_2]X_2 + 2R' = [Me(Ant)_2]R_2 + 2X', \qquad (2)$$

where X = Cl', CH_3COO' or NO_3' and R' = CNS', Br' or I'.

EXPERIMENTAL

The calculated amounts of reactants were used for the most part in the synthesis of antipyrine complexes, and were dissolved in a small amount of water. The solutions were mixed and a precipitate came down at once or after a short time.

Synthesis of diantipyrinecadmium thiocyanate: No success attended efforts to prepare diantipyrinecadmium thiocyanate by the action of a nitrate, chloride, or sulfate of cadmium with the thiocyanate of an alkali metal (NH_4CNS or KCNS), followed by reaction with a solution of antipyrine; i.e. it was impossible to effect substitution of one anion by another (CNS') in the outer sphere: (see equation 2). Cadmium carbonate was therefore first prepared from pure cadmium sulfate. Cadmium thiocyanate was prepared by reacting an excess of cadmium carbonate with freshly prepared thiocyanic acid. The so-prepared cadmium thiocyanate was recrystallized several times and 1.70 g of it was dissolved in 25 ml water. Both solutions were heated to 70° and then mixed. After a short time a crystalline precipitate was formed. The product was recrystallized and dried at 100°.

0.2560 g substance: 0.0874 g $CdSO_4$. 0.2480 g substance: 0.0850 g $CdSO_4$. 0.2000 g substance: 25 ml 0.1 N iodine (K = 0.98560); 11.5 ml 0.1 N $Na_2S_2O_3$; 0.1236 g antipyrine.[1] 0.2000 g substance; 25 ml 0.1 N iodine (K = 0.98560); 11.4 ml 0.1 N $Na_2S_2O_3$; 0.1245 g antipyrine. 0.2268 g substance: 0.1262 g AgCNS. 0.2068 g substance: 0.1138 g AgCNS. Found %: Cd 18.41, 18.48; antipyrine 61.80, 62.25; CNS 19.47, 19.25. $[Cd(Ant)_2](CNS)_2$. Calculated %: Cd 18.59; antipyrine 62.20; CNS 19.21.

Preparation of diantipyrinezinc thiocyanate. The synthesis was effected on the basis of ion exchange between zinc sulfate and ammonium thiocyanate followed by reaction with antipyrine solution. The reaction took place according to the equation:

$$ZnSO_4 + 2NH_4CNS + 2Ant = [Zn(Ant)_2](CNS)_2 + (NH_4)_2SO_4.$$

0.20 g zinc sulfate was dissolved in 50 ml aqueous solution containing 0.25 g antipyrine, and to the resultant solution was gradually added 10 ml ammonium thiocyanate solution containing about 0.20 g substance. Almost immediately a white precipitate came down which changed on heating into a resinous mass, but after a short period was transformed into a crystalline material. The product was recrystallized from water several times and dried at 75-80°.

0.2542 g substance: 0.0629 g $Zn_2P_2O_7$. 0.2508 g substance: 0.0624 g $Zn_2P_2O_7$. 0.1870 g substance: 25 ml 0.1 N iodine (K = 0.98560); 11.05 ml 0.1 N $Na_2S_2O_3$; 0.1278 g antipyrine. 0.1980 g substance: 25 ml 0.1 N iodine (K = 0.98560); 11.04 ml 0.1 N $Na_2S_2O_3$; 0.1279 g antipyrine. 0.2114 g substance: 0.1236 g AgCNS, 0.2168 g substance: 0.1272 g AgCNS. Found %: Zn 10.61, 10.67; antipyrine 68.34, 68.40; CNS 20.46, 20.53. $[Zn(Ant)_2](CNS)_2$. Calculated %: Zn 10.72; antipyrine 68.46; CNS 20.82.

Preparation of diantipyrinezinc chloride. The synthesis was effected in the following manner: 5 g fused zinc chloride was dissolved in 5 ml water, the solution filtered from the resultant small residue (hydrolysis) and addition made of about 25 ml of 8% aqueous solution of antipyrine. The precipitate was filtered, dissolved in 25 ml hot water and recrystallized. After a few recrystallizations the product was dried at 75-80°.

[1]) Antipyrine was determined iodometrically as follows: A weighed sample was dissolved in 25 ml water and to the solution was added about 5 g crystalline sodium acetate and 25 ml 0.1 N iodine solution. After 20 minutes about 50 ml alcohol was added and the iodine back-titrated with 0.1 N solution of $Na_2S_2O_3$ (1 ml 0.1 N iodine solution is equivalent to 0.009405 g antipyrine).

0.4000 g substance: 0.1194 g $Zn_2P_2O_7$. 0.3868 g substance: 0.1144 g $Zn_2P_2O_7$. 0.1940 g substance: 25 ml 0.1 N iodine (K = 0.98560); 9.5 ml 0.1 N $Na_2S_2O_3$; 0.1424 g antipyrine. 0.1910 g substance: 25 ml 0.1 N iodine (K = 0.98560); 9.7 ml 0.1 N $Na_2S_2O_3$; 0.1404 g antipyrine. 0.1932 g substance: 0.1044 g AgCl. 0.1566 g substance: 0.0906 g AgCl. Found %: Zn 12.80, 12.70; antipyrine 73.40, 73.50; Cl 13.40, 14.31. $[Zn(Ant)_2]Cl_2$. Calculated %: Zn 12.76; antipyrine 73.40; Cl 13.84.

The properties of the prepared compounds are listed in Table 1.

Table 1

Properties \ Formula	$[Cd(Ant)_2](CNS)_2$	$[Zn(Ant)_2](CNS)_2$	$[Zn(Ant)_2]Cl_2$
Color of crystals	White	White	White
Behavior in air	Stable	Stable	Stable
Solubility in water at 15°	1.0 g : 100 ml	0.40 g : 100 ml	1.70 g : 100 ml Vitreous mass formed when evaporated.
Ditto in C_2H_5OH	0.74 g: 100 ml	0.32 g : 100 ml	0.44 g : 100 ml
Ditto in $(C_2H_5)_2O$	0.076 g: 100 ml	0.14 g : 100 ml	0.23 g : 100 ml
Behavior of satd. solns. towards conc. H_2SO_4 and HNO_3	No change with H_2SO_4. With HNO_3 the dry substance develops a pink color changing to yellow.		No change with H_2SO_4, with HNO_3 it gives a yellow color changing to dark red.
Ditto towards 1 N NaOH solution	White pp. of $Cd(OH)_2 \cdot NH_4OH$ formed. NH_4OH gives white pp. of $Cd(OH)_2$, sol. in excess of reagent	White pp. of $Zn(OH)_2$ is formed, soluble in excess of reagent	
Ditto towards 0.1 N $AgNO_3$ soln.	Slightly turbid solution; addition of HNO_3 increases the pp.		
Ditto towards $NaNO_2$ soln.	Acidification with H_2SO_4 gives the greenish color of nitrosoantipyrine		
Ditto towards weak $FeCl_3$ soln.	Red coloration		Red color--due to ferropyrine
Behavior of dry substance on heating in a capillary	Melts at 140°	Melts at 115°	Melts at 157°
Electric conductivity at 15°	μ_{1000}205; μ_{2000}232	μ_{1000}202; μ_{2000}230	μ_{1000}223; μ_{2000}239
Appearance of crystals under microscope	Figs. 1 and 2 [1]	Fig. 3	Figs. 4 and 5

Preparation of diantipyrinezinc bromide. Zinc bromide was first prepared by reaction of metallic zinc with bromine. To 40 ml freshly prepared solution of zinc bromide was added in the cold 40 ml antipyrine solution. In addition to a crystalline precipitate a small quantity of flocculent material was obtained. The solution containing the precipitate was heated when the whole of the latter dissolved; on then cooling, crystals came down. The product was recrystallized

[1] Figures 1 to 12 are enlarged 120 times. See Plate, p. 2349.

several times and dried at 80°.

0.4074 g substance: 0.1020 g $Zn_2P_2O_7$. 0.4004 g substance: 0.1006 g $Zn_2P_2O_7$. 0.1850 g substance: 25 ml 0.1N iodine (K=0.98560); 12.35 ml 0.1 N $Na_2S_2O_3$; 0.1156 g antipyrine. 0.1800 g substance: 25 ml 0.1 N iodine (K=0.98560); 12.65 ml 0.1 N $Na_2S_2O_3$; 0.1127 g antipyrine. 0.1958 g substance: 0.1234 g AgBr. 0.2114 g substance: 0.1344 g AgBr. Found %: Zn 10.74, 10.78; antipyrine 62.49, 62.61; Br 26.82, 27.05. $[Zn(Ant)_2]Br_2$. Calculated %: Zn 10.87; antipyrine 62.55; Br 26.58.

Preparation of diantipyrinecadmium bromide. To a hot solution of 2.80 g cadmium bromide in 25 ml water was added 25 ml of a hot solution of 3.80 g antipyrine. After 24 hours the crystalline precipitate was filtered off, recrystallized from hot water and dried at 75-80°.

0.3236 g substance: 0.1044 g $CdSO_4$. 0.4084 g substance: 0.1321 g $CdSO_4$. 0.2084 g substance; 25 ml 0.1 N iodine (K=0.98560); 11.80 ml 0.1 N $Na_2S_2O_3$; 0.1209 g antipyrine. 0.1846 g substance: 25 ml 0.1 N iodine (K=0.98560); 13.25 ml 0.1 N $Na_2S_2O_3$; 0.1072 g antipyrine. 0.2100 g substance: 0.1228 g AgBr. 0.2076 g substance: 0.1180 g AgBr. Found %: Cd 17.40, 17.44; antipyrine 58.02, 58.08; Br 24.89, 24.19. $[Cd(Ant)_2]Br_2$. Calculated %: Cd 17.33; antipyrine 57.75; Br 24.92.

The properties of diantipyrinezinc bromide and diantipyrinecadmium bromide are given in Table 2.

Table 2

Properties \ Formula	$[Zn(Ant)_2]Br_2$	$[Cd(Ant)_2]Br_2$
Color of crystals	White	White
Behavior in air	Stable	
Solubility in water at 15°	2.10 g: 100 ml	1.16 g: 100 ml
Ditto in C_2H_5OH	0.48 g: 100 ml	0.51 g: 100 ml
Ditto in $(C_2H_5)_2O$	Insoluble	0.076 g: 100 ml
Behavior of saturated solutions toward H_2SO_4 and HNO_3 in the cold	No change in presence of dilute acid. Conc. HNO_3 gradually decomposes the dry substance with liberation of bromine.	
Ditto toward NaOH (1 N)	Formation of pp. of $Zn(OH)_2$ soluble in excess of reagent	Formation of pp. of $Cd(OH)_2$
Ditto toward $AgNO_3$ soln. (0.1 N)	Pp. of AgBr is formed and becomes larger when HNO_3 is added.	
Ditto toward dilute $FeCl_3$ soln.	Red coloration developed, due to ferropyrine.	
Behavior of dry substance on heating in a capillary	Melts at 192.5°	Melts at 144°
Electrical conductivity at 15°	μ_{1000} 236; μ_{2000} 249	μ_{1000} 214; μ_{2000} 219
Appearance of crystals under the microscope	Figures 6 and 7	Figures 8 and 9

Preparation of diantipyrinezinc iodide. Zinc iodide was first prepared by treating metallic zinc with iodine. To 50 ml of a 12% boiling aqueous solution of antipyrine was gradually added 10 ml of freshly prepared solution containing 5 g zinc iodide. The resultant precipitate was a white resinous mass which after a

short time changed into a crystalline mass. It was recrystallized and dried at 80°.

0.4074 g substance: 0.0904 g $Zn_2P_2O_7$. 0.3892 g substance: 0.0856 g $Zn_2P_2O_7$. 0.1986 g substance: 25 ml 0.1 N iodine (K=0.98560); 13.22 ml 0.1 N $Na_2S_2O_3$; 0.1074 g antipyrine. 0.2054 g substance; 25 ml 0.1 N iodine (K=0.98560); 12.82 ml 0.1 N $Na_2S_2O_3$; 0.1112 g antipyrine. 0.2200 g substance: 0.1488 g AgI. 0.1994 g substance: 0.1354 g AgI. Found %: Zn 9.51, 9.44; antipyrine 54.09, 54.15; I 36.56; 36.71. $[Zn(Ant)_2]I_2$. Calculated %: Zn 9.40; antipyrine 54.10; I 36.50.

Preparation of diantipyrinecadmium iodide. To 50 ml of solution containing 9.20 g cadmium iodide was added 50 ml of 5% antipyrine solution. A white crystalline precipitate was at once formed. It was recrystallized several times and dried at 80°.

0.3060 g substance: 0.0856 g $CdSO_4$. 0.2974 g substance: 0.0834 g $CdSO_4$. 0.1842 g substance: 25 ml 0.1 N iodine (K=0.98560); 14.70 ml 0.1 N $Na_2S_2O_3$; 0.0935 g antipyrine. 0.1906 g substance: 25 ml 0.1 N iodine (K=0.98560); 14.37 ml 0.1 N $Na_2S_2O_3$; 0.0966 g antipyrine. 0.2464 g substance: 0.1562 g AgI. 0.2360 g substance: 0.1498 g AgI. Found %: Cd 15.08, 15.12; antipyrine 50.75, 50.70; I 34.27, 34.23. $[Cd(Ant)_2]I_2$. Calculated %: Cd 15.14; antipyrine 50.67; I 34.19.

The properties of diantipyrinezinc iodide and diantipyrinecadmium iodide are given in Table 3.

Table 3

Properties \ Formula	$[Zn(Ant)_2]I_2$	$[Cd(Ant)_2]I_2$
Color of crystals	White	White
Behavior in air	Stable	Stable
Solubility in water at 15°	0.65 g: 100 ml	0.31 g: 100 ml
Ditto in C_2H_5OH	0.63 g: 100 ml	4.74 g: 100 ml
ditto in $(C_2H_5)_2O$	0.036 g: 100 ml	0.096 g: 100 ml
Behavior of saturated solns toward H_2SO_4 and HNO_3	Dilute acids have no action, Conc. HNO_3 decomposes the dry substance with liberation of iodine	
Ditto toward NaOH soln. (1.0 N)	Formation of white pp. of $Zn(OH)_2$ soluble in excess of reagent	Pp. of $Cd(OH)_2$
Ditto towards $AgNO_3$ soln. (0.1 N)	Forms white pp. of AgI	
Ditto towards dilute soln of $FeCl_3$	Yellowish-red color - due to ferropyrine. Conc.soln of $FeCl_3$ gives a cherry-red color	
Behavior of dry substance when heated in a capillary	Melts at 171°	Melts at 136.5°
Electric conductivity at 15°	.....	.....
Appearance of crystals under microscope	Figures 10 and 11	Figure 12

It should be pointed out in conclusion that the most difficultly soluble of the obtained compounds are diantipyrinezinc iodide and diantipyrinecadmium iodide. The melting points of all the complex compounds are higher than the melting point of antipyrine.

On the basis of a study of the molecular electric conductivity, all the synthesized compounds consist of ternary electrolytes, i.e. they dissociate into three ions according to the equation:

$$[Me^{2+}(Ant)_2]X_2 \rightleftarrows [Me^{2+}(Ant)_2]^{2+} + 2X'.$$

SUMMARY

1. Antipyrine in neutral solution can penetrate the molecule of certain iodides, bromides, chlorides and thiocyanates of bivalent metals to form compounds with the general formula $[Me(Ant)_2]X_2$.

2. These compounds can be prepared by direct reaction of a solution of antipyrine with the salt of the bivalent metal; but the syntheses of the complexes by double decomposition of the salts in presence of antipyrine proceeds with greater difficulty or not at all.

3. Seven complexes of zinc and cadmium with antipyrine were synthesized and some of their properties investigated.

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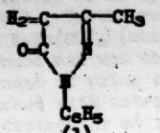
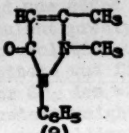
THE REACTION OF SOME PYRAZOLE DERIVATIVES WITH THE ION OF TRIVALENT IRON AND WITH CYANIDE COMPLEXES

S. I. Gusev and R. G. Beiles

It is known that Fe^{3+} and $[Fe(CN)_6]^{-3}$ ions do not form a precipitate in aqueous solutions. In the presence, however, of phenylmethyl pyrazolone (1) or antipyrine (2)



(1)



(2)

a dark-red precipitate immediately comes down; according to analytical data this possesses the formula (I) (in the case of the antipyrine derivative):

$$[Fe^{3+}(C_{11}H_{12}ON_2)_3]^{3+}[Fe^{3+}(CN)_6]^{3-}\cdot 3H_2O. \qquad (I)$$

The obtained compound thus resembles the so-called ferropyrine in structure and differs from the latter in respect of the anion. The existence of compound (I) aroused our interest in connection with the fact that Ryabchikov and Terenteva in a study of the antipyrine complexes of trivalent rare-earth metals [1] had been unable to prepare compounds containing the $[Fe(CN)_6]^{3-}$ ion, although they succeeded in synthesizing a series of compounds containing other anions, such as $[Pr(C_{11}H_{12}ON_2)_6][Cr(CNS)_6]$. We may note that in all compounds of trivalent rare-earth metals the central atom is coordinated around 6 molecules of antipyrine.

During an investigation of the above-mentioned reaction between Fe^{3+}, antipyrine and cyanide anions, we observed also that the reaction takes place not only with the $[Fe(CN)_6]^{3-}$ ion but also with several other cyanide complex anions with a trivalent central atom. The following substances were prepared in addition to the one described:

$$[Fe^{3+}(C_{11}H_{12}ON_2)_3]_2^{3+}[Fe^{3+}(CN)_5NO]_3^{2-}\cdot 3H_2O, \qquad (II)$$

$$[Fe^{3+}(C_{11}H_{12}ON_2)_3]_2^{3+}[Fe^{3+}(CN)_5NH_3]_3^{2-}\cdot 12H_2O, \qquad (III)$$

$$[Fe^{3+}(C_{11}H_{12}ON_2)_3]^{3+}[Co^{3+}(CN)_6]^{3-}\cdot 4H_2O. \qquad (IV)$$

Cobalt enters into the composition of the latter compound. It may be suggested that this reaction is a general one for cyanide anions containing a trivalent central atom. In these compounds one and the same atom -- trivalent iron -- is a complex former both as a cation and an anion. The theory may be advanced that some of the H_2O molecules enter the inner sphere of the cation, so that the central Fe^{3+} atom in these compounds has a coordination number of 6, as for instance $[Fe(C_{11}H_{12}ON_2)_3\cdot 3H_2O][Fe(CN)_6]$. Conflicting with this theory, however, is the existence of the compound

$$[Fe(C_{11}H_{12}ON_2)_3]_2[Fe(CN)_5NO]_3\cdot 3H_2O.$$

We are therefore inclined to ascribe to the compounds which we have prepared the structure represented in formulas (I), (II), (III), and (IV). Consequently we have an interesting example of compounds in which both the cation and the anion of the complex formers are one and the same atoms (Fe^{3+}) but the latter possess different coordination numbers (3 for the cation and 6 for the anion).

All the substances which we have prepared consist of red precipitates of different shades, not exhibiting a crystalline structure under the microscope. The freshly prepared compounds are fairly readily soluble in water and alcohol, but after drying (even at room temperature) their solubility is sharply reduced, possibly due to irreversible loss of part of the water of crystallization.

EXPERIMENTAL

Preparation of ferropyrine ferricyanide (I). To 20 ml of 5% aqueous solution of antipyrine[1] (1 g) was added 0.2 g $Fe_2(SO_4)_3$ solution in 5 ml water. To the resultant dark-red liquid was added gradually a 5% solution of $K_3Fe(CN)_6$ (about 6 ml). A red flocculent precipitate was immediately formed and was able to redissolve in the solution on addition of a large amount of water or alcohol. The precipitate was filtered off, carefully washed with water until the reaction for SO_4 ion was negative, and dried in a desiccator at room temperature to constant weight. It was dried at 100-105° for determination of the water of crystallization and for analysis.

1.2 g of dry product was prepared in the form (after pulverizing) of a dark-red powder. The iron was determined by the permanaganate method after mineralization of the substance with a few milliliters of concentrated sulfuric acid and reduction of the Fe^{3+} to Fe^{2+}. The inaccuracy of some analyses may be explained by the impossibility of purifying the compounds by recrystallization or other methods.

Determination of water of crystallization. 0.5742 g substance: Weight after drying 0.5380 g. Found %: H_2O 6.30. $[Fe(C_{11}H_{12}ON_2)_3][Fe(CN)_6]\cdot 3H_2O$. Calculated %: H_2O 6.10.

4.575 mg substance: 0.7938 ml N_2 (18°, 733 mm). 2.940 mg substance: 0.5096 ml N_2 (19°, 733 mm). 0.2112 g substance: 4.95 ml 0.1 N $KMnO_4$ (K = 1.0052). 0.2006 g substance: 4.75 ml 0.1 N $KMnO_4$ (K = 1.0052). Found %: N 19.63, 19.54; Fe 13.16, 13.29. $C_{36}H_{36}N_{12}O_3Fe_2$. Calculated %: N 20.20; Fe 13.41.

On the basis of the data obtained the formation of ferropyrine ferrocyanide (I) may be represented by the following equation:

$$3C_{11}H_{12}ON_2 + Fe^{3+} + [Fe(CN)_6]^{3-} = [Fe^{3+}(C_{11}H_{12}ON_2)_3]^{3+}[Fe(CN)_6]^{3-}.$$

The substance (anhydrous complex) is poorly soluble in water, but after keeping for a prolonged period it gradually hydrolyzes. Hydrolysis proceeds more rapidly in presence of weak acids, especially when heated, as reflected in the intensification of the positive reaction for the Fe^{3+} ion with $K_4Fe(CN)_6$; on addition to the precipitate of 1 N NaOH, flocs of $Fe(OH)_3$ separated out. With $FeSO_4$ the solution acquires the dark-blue color of Turnbull's blue, thus confirming the presence of the $[Fe(CN)_6]^{3-}$ ion; Fe^{3+} did not provoke any change in the precipitate.

The air-dry complex decreases slightly in volume at 95°; above 170° it sinters with decomposition. In alcohol a green-gray solution is formed with concentration of 0.1%.

Preparation of ferropyrine nitroprusside (II). Amounts used were 20 ml of 5% antipyrine solution, 10 ml $Fe_2(SO_4)_3$ solution (0.3 g) and 10 ml of 5% solution of sodium nitroprusside. Complex formation proceeded on the same lines as before. The substance resembles product (I) in properties, except for the reactions characterizing the $[Fe(CN)_6]^{3-}$ ion.

Determination of water of crystallization. 0.5558 g substance: after drying the weight was 0.5396 g. Found %: H_2O 2.92.
$[Fe(C_{11}H_{12}ON_2)_3]_2[Fe(CN)_5NO]_3\cdot 3H_2O$. Calculated %: H_2O 2.78.

[1]) All the syntheses proceed in the same way with phenylmethyl pyrazolone as with antipyrine, except that an alcoholic solution of the base is used instead of an aqueous one.

3.516 mg substance: 0.6546 ml N_2 (19°, 734 mm). 5.576 mg substance: 1.0339 ml N_2 (19°, 733 mm). Found %: N 21.03, 20.91; Fe 14.30, 14.42. 0.1982 g substance 5.05 ml 0.1 N $KMnO_4$ (K = 1.0052). 0.1888 g substance: 4.85 ml 0.1 N $KMnO_4$ (K = 1.0052). $C_{81}H_{71}N_{30}O_9Fe_3$. Calculated %: N 22.24; Fe 14.78.

On the basis of the obtained data the reaction of formation of ferropyrine nitroprusside may be represented by the following equation:

$$6C_{11}H_{12}ON_2 + 2Fe^{3+} + 3[Fe(CN)_5NO]^{2-} = [Fe^{3+}(C_{11}H_{12}ON_2)_3]_2[Fe^{3+}(CN)_5NO]_3.$$

Preparation of ferropyrine pentacyanoamminoferrate (III). The preparation was first carried out of $Na_2NH_4[Fe^{2+}(CN)_5NH_3]$, which was oxidized by sodium nitrite in an acid medium to $Na_2[Fe^{3+}(CN)_5NH_3]$ [2]. A solution of 1 g of the latter substance in 15 ml water was gradually added to a solution of ferropyrine (not the ferropyrine to the sodium salt), when a reddish-brown precipitate was formed. After filtering, washing, drying and pulverizing, there was obtained 0.7 g of brownish-red powder. The substance blackens after prolonged standing in the air. The air-dry product contains 12 molecules of water of crystallization.

Determination of water of crystallization. 0.6620 g substance: weight after drying 0.5944 g. Found %: H_2O 10.21. $[Fe(C_{11}H_{12}ON_2)_3][Fe(CN)_5NH_3]\cdot 12H_2O$. Calculated %: H_2O 10.40. 6.330 mg substance: 1.267 ml N_2 (23°, 731 mm). 4.300 mg substance: 0.8866 ml N_2 (23°, 731 mm). 0.2098 g substance: 5.50 ml 0.1 N $KMnO_4$ (K = 1.0052). 0.1950 g substance: 5.15 ml 0.1 N $KMnO_4$ (K = 1.0052). Found %: N 22.20, 22.35; Fe 14.75, 14.86. $C_{81}H_{81}O_6N_{30}Fe_3$. Calculated %: N 22.71; Fe 15.10.

Preparation of ferropyrine hexacyanocobaltate (IV). To 2.5 g antipyrine in 50 ml water was added a solution of 1.5 g ferric ammonium sulfate in 10 ml water, followed by 2 g $Na_3[Co(CN)_6]$ in 30 ml water. The dark-red precipitate was filtered off, carefully washed, dried, and pulverized. Yield 3.0 g. The air-dry product contains 4 molecules of water of crystallization.

For analysis, a weighed sample was heated in a Kjeldahl flask in presence of concentrated sulfuric acid, and the iron was separated by the acetate method, dissolved in HCl and estimated as Fe_2O_3. The cobalt in the solution was brought down by α-nitroso-β-naphthol and determined as Co_3O_4.

Determination of water of crystallization. 0.8382 g substance; weight after drying 0.7694 g. Found %: H_2O 8.21. $[Fe(C_{11}H_{12}ON_2)_3][Co(CN)_6]\cdot 4H_2O$. Calculated %: H_2O 7.94. 4.590 mg substance: 0.8069 ml N_2 (21°, 732 mm). 5.210 mg substance: 0.9743 ml N_2 (21°, 732 mm). 0.3700 g substance: 0.0336 g Fe_2O_3. 0.3250 g substance: 0.0290 g Fe_2O_3. 0.3700 g substance: 0.0352 g Co_3O_4. 0.3250 g substance: 0.0314 g Co_3O_4. Found %: N 19.66, 19.84; Fe 6.35, 6.24; Co 6.98, 7.09. $C_{39}H_{36}N_{12}O_3FeCo$. Calculated %: N 20.12; Fe 6.68; Co 7.05.

SUMMARY

Compounds (I), (II), (III), and (IV) were prepared by reaction of antipyrine with Fe^{3+} and the cyanide anions: $[Fe(CN)_6]^{3-}$, $[Fe(CN)_5NO]^{2-}$, $[Fe(CN)_5NH_3]^{2-}$ and $[Co(CN)_6]^{3-}$. Similar products are formed by 1-phenyl-3-methylpyrazolone-5.

Iron functions as the central atom both in the cations and the anions (except in compound (IV) which contains Co in the anion).

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PHOTOREACTIONS OF ORGANOIODINE COMPOUNDS

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In one of our investigations [1] it was shown that ArHgI and diphenyl are formed by the action of ultraviolet light on Ar_2Hg and iodobenzene in benzene solution, whereas in alcoholic solution ArHgI and benzene are formed. Irradiation of Ar_2Hg and benzyl iodide in alcohol and in benzene yields ArHgI and dibenzyl. A scheme was proposed for this type of reaction which involved the dissociation of Ar_2Hg during the action of light on the radicals, the latter subsequently reacting with each other and with the solvent:

$$Ar_2Hg \xrightarrow{h\nu} ArHg\cdot + Ar\cdot, \quad (1)$$

$$RI \xrightarrow{h\nu} R\cdot + I\cdot, \quad (2)$$

$$ArHg\cdot + I\cdot \longrightarrow ArHgI, \quad (3)$$

$$R\cdot + R\cdot \longrightarrow RR, \quad (4)$$

$$Ar\cdot + Ar\cdot \longrightarrow ArAr, \quad (5)$$

$$2R\cdot + CH_3OH \longrightarrow 2RH + CH_2O, \quad (6)$$

$$2Ar\cdot + CH_3OH \longrightarrow 2ArH + CH_2O. \quad (7)$$

Reactions (4) and (5) proceed in benzene solution, reactions (6) and (7) in alcoholic solution. In all cases the benzyl radical dimerizes to dibenzyl, which is in full accord with the previously obtained results [2] on the behavior of the benzyl radical during the photoreactions of mercury dibenzyl.

In a further check on this scheme we have investigated the photoreactions of mercury dibenzyl with iodobenzene in solution in methyl alcohol and benzene. Here the origin of the radicals is different from that in the above-enumerated reactions: the benzyl radical is formed by photolysis of mercury dibenzyl and the phenyl radical by photolysis of iodobenzene. In this case, in harmony with the proposed mechanism, the benzyl radical dimerizes to dibenzyl, while the phenyl radical and atomic iodine add on to mercury with formation of phenyl mercuric iodide. Formation of HgI_2, benzene or diphenyl proceeded to some extent:

$$(C_6H_5CH_2)_2Hg \xrightarrow{h\nu} C_6H_5CH_2\cdot + Hg,$$

$$C_6H_5I \xrightarrow{h\nu} C_6H_5\cdot + I\cdot,$$

$$C_6H_5\cdot + I\cdot + Hg \longrightarrow C_6H_5HgI,$$

$$2C_6H_5CH_2\cdot \longrightarrow C_6H_5CH_2CH_2C_6H_5,$$

$$2C_6H_5\cdot + CH_3OH \longrightarrow 2C_6H_6 + CH_2O,$$

$$2C_6H_5\cdot \longrightarrow C_6H_5C_6H_5 \quad \text{(in benzene)}.$$

We account for the formation of phenyl mercuric iodide by reaction of a phenyl radical and an iodine atom with the metallic mercury liberated during photolysis of dibenzyl mercury.

To verify this scheme experiments were performed on the interaction of iodobenzene with metallic mercury during irradiation with ultraviolet light in solution in methyl alcohol and benzene. Here again phenyl mercuric iodide was formed side by side with mercuric iodide:

$$C_6H_5I + Hg \xrightarrow{h\nu} C_6H_5HgI$$

This reaction consequently constitutes a broadening of the synthesis of organomercury compounds from organoiodine compounds and mercury first performed by Zinin [3] who worked with unsaturated organoiodine compounds.

Alkyl derivatives of mercury can also be prepared by irradiation of alkyl iodide and mercury [4], and also benzyl mercuric iodide from benzyl iodide and mercury [5].

The formation of aryl mercuric iodides from aryl iodide and mercury is also the subject of our investigation.

The photoreaction of dibenzyl mercury was also carried out with methyl iodide in solution in benzene and alcohol. Once again in both cases the benzyl radical dimerized to dibenzyl, and mercuric iodide was formed, while the methyl radical reacted with the alcohol to form methane and formaldehyde; in benzene solution, however, the methyl radical dimerized to ethane. We failed to observe the formation of methyl mercuric iodide, contrary to what might have been expected from the analogy with the previously described reactions.

The photoreactions of iodobenzene with R_2Hg were extended to alkyl derivatives of mercury. Experiments were undertaken with dimethyl mercury and iodobenzene in a solution of methyl alcohol and benzene, and also with diethyl mercury and iodobenzene in methyl alcohol. The reaction proceeded according to a scheme similar to the one previously advanced for aryl derivatives of mercury.

In both solvents dimethyl mercury gave methyl mercuric iodide. The methyl and phenyl radicals reacted with the alcohol to give, respectively, methane or benzene and formaldehyde. In the benzene solution, however, the radicals dimerized to diphenyl and ethane:

$$(CH_3)_2Hg \xrightarrow{h\nu} CH_3Hg\cdot + CH_3\cdot,$$

$$C_6H_5I \xrightarrow{h\nu} C_6H_5\cdot + I\cdot,$$

$$CH_3Hg\cdot + I\cdot \longrightarrow CH_3HgI,$$

$$2CH_3\cdot + CH_3OH \longrightarrow 2CH_4 + CH_2O,$$

$$2C_6H_5\cdot + CH_3OH \longrightarrow 2C_6H_6 + CH_2O,$$

$$2CH_3\cdot \longrightarrow CH_3CH_3 \text{ (in benzene)},$$

$$2C_6H_5\cdot \longrightarrow C_6H_5C_6H_5 \text{ (in benzene)}.$$

Diethyl mercury in alcoholic solution reacted with iodobenzene to form ethyl mercuric iodide, benzene, ethane and ethylene, which resulted from the disproportionation of the free ethyl radical:

$$(C_2H_5)_2Hg \xrightarrow{h\nu} C_2H_5Hg\cdot + C_2H_5\cdot,$$

$$C_6H_5I \xrightarrow{h\nu} C_6H_5\cdot + I\cdot,$$

$$C_2H_5Hg\cdot + I\cdot \longrightarrow C_2H_5HgI,$$

$$2C_2H_5\cdot \longrightarrow C_2H_6 + C_2H_4,$$

$$2C_6H_5\cdot + CH_3OH \longrightarrow 2C_6H_6 + CH_2O.$$

In order to verify the foregoing schemes, diphenyl mercury was reacted with methyl iodide in alcoholic solution when the anticipated products -- phenyl mercuric iodide, methane, benzene, and formaldehyde -- were obtained:

$$(C_6H_5)_2Hg \xrightarrow{h\nu} C_6H_5Hg\cdot + C_6H_5\cdot,$$

$$CH_3I \xrightarrow{h\nu} CH_3\cdot + I\cdot,$$

$$C_6H_5Hg\cdot + I\cdot \longrightarrow C_6H_5HgI,$$

$$2C_6H_5\cdot + CH_3OH \longrightarrow 2C_6H_6 + CH_2O,$$

$$2CH_3\cdot + CH_3OH \longrightarrow 2CH_4 + CH_2O.$$

The above reactions of phenyl radicals with mercury in solutions are similar in mechanism to the previously described reactions of diazonium salts and of diphenyliodinium chloride with mercury to which we drew attention in a previous publication [6].

In the foregoing schemes for the primary process we had assumed that RI dissociates into R· and I·. Consequently if a compound were to be introduced into the reaction which could combine with the released iodine, then we should have a system containing free R radicals. We selected antimony triphenyl as an example of a suitable iodine acceptor; this compound is not decomposed when its solutions are exposed to ultraviolet light [7]. It was actually found that on irradiating solutions of iodobenzene in presence of triphenyl antimony, the latter reacts with the liberated iodine to form triphenyl antimony diiodide. This reaction again confirms the scheme submitted above for the mechanism of the reaction involving free radicals, since the ionic dissociation of iodobenzene would have led us to expect the formation of stibonium salts:

$$(C_6H_5)_3Sb + C_6H_5^{(+)} + I^{(-)} \longrightarrow (C_6H_5)_4Sb^{(+)} + I^{(-)}.$$

Therefore the system $(C_6H_5)_3Sb + C_6H_5I$ gives the free radicals:

$$(C_6H_5)_3Sb + 2C_6H_5I \longrightarrow (C_6H_5)_3SbI_2 + 2C_6H_5\cdot.$$

We studied the photoreactions of triphenyl antimony with iodobenzene in various solvents. The liberated phenyl radical reacted with the solvent in precisely the same manner as the phenyl radical which was obtained in the photolysis of diphenyl mercury [8]. Benzene was formed in methyl alcohol and chloroform at the expense of hydrogen from the solvent, while in benzene solution dimerization to diphenyl took place:

$$(C_6H_5)_3Sb + 2C_6H_5I \xrightarrow{h\nu} (C_6H_5)_3SbI_2 + 2C_6H_5\cdot,$$

$$2C_6H_5\cdot + CH_3OH \longrightarrow 2C_6H_6 + CH_2O,$$

$$C_6H_5\cdot + CHCl_3 \longrightarrow C_6H_6 + CCl_3\cdot,$$

$$2CCl_3\cdot \longrightarrow CCl_3CCl_3.$$

Triphenyl antimony and methyl iodide react similarly to give triphenyl antimony diiodide and a methyl radical, the latter reacting further with the methyl alcohol to give methane and formaldehyde.

EXPERIMENTAL

Photoreaction of triphenyl antimony with iodobenzene in methyl alcohol. A solution comprising 1.5 g triphenyl antimony, 1.7 g iodobenzene and 20 ml methyl alcohol was irradiated for about 60 hours with a PRK-2 quartz mercury lamp. The solvent was distilled off, diluted with water and extracted with carbon tetrachloride for removal of the benzene which on nitration gave 0.3 g m-dinitrobenzene with m.p. 89° (no depression of m.p. of the pure substance). The formaldehyde in the aqueous alcoholic solution was detected by the silver mirror and resorcinol reactions.

The residue of triphenyl antimony diiodide, amounting to 1 g (35% of theory), isolated after distilling off the solvent, was converted into triphenyl antimony dihydroxide by the following method: the triphenyl antimony diiodide was introduced into an alcoholic solution of potassium hydroxide, the mixture boiled until

the reaction was completed, the precipitated potassium iodide was filtered off, the excess of potassium hydroxide removed by a stream of carbon dioxide, and the solution evaporated to dryness. The residue was treated with ether, after which it was converted into a powder and dissolved in glacial acetic acid. Addition to the solution of a large quantity of water led to the separation of triphenyl antimony dihydroxide in the form of a light powder, insoluble in ether and melting at 206-208°. The products of the reaction were therefore triphenyl antimony diiodide, benzene and formaldehyde.

Photoreaction of triphenylantimony with iodobenzene in benzene. A solution of 1.5 g triphenyl antimony, 1.7 g iodobenzene and 20 ml benzene was irradiated for about 60 hours. After distillation of the solvent, 0.1 g diphenyl was isolated from the residue by steam distillation. M.p. 70° (no depression of m.p. of pure specimen). The residue was extracted with ether to give 1.2 g (70% of theory) triphenyl antimony dihydroxide with m.p. 208-209°. The reaction products were accordingly triphenylantimony diiodide and diphenyl.

Photoreaction of triphenylantimony with iodobenzene in chloroform. A solution comprising 1.5 g triphenyl antimony, 1.7 g iodobenzene and 20 ml chloroform was irradiated for about 60 hours. The chloroform was distilled off and the residue nitrated to give 0.15 g m-dinitrobenzene with m.p. 90° (no depression of m.p. of pure product). Steam distillation of the residue after removal of the solvent gave hexachlorethane with m.p. 181-182° in a sealed capillary (no depression with a mixed sample). The reaction products were therefore triphenylantimony diiodide, benzene and hexachlorethane.

Photoreaction of dibenzyl mercury with iodobenzene in alcohol. A solution comprising 1.2 g dibenzyl mercury, 0.6 g iodobenzene and 20 ml methyl alcohol was irradiated for about 50 hours. The resultant precipitate was filtered off and weighed. Its weight was 0.9 g. Extraction with ethylene dichloride removed 0.6 g (60% of theory) of phenyl mercuric iodide with m.p. 273° (no depression of m.p. of pure specimen). The remaining 0.3 g of precipitate proved to be mercuric iodide when subjected to various tests. The methyl alcohol was distilled off from the filtrate and diluted with water when the benzene separated out. The latter was removed with carbon tetrachloride and nitrated. An insignificant amount of m-dinitrobenzene was obtained with m.p. 89° (no depression in mixed melting test). The residue after distillation of the methyl alcohol was distilled with steam to give 0.4 g dibenzyl with m.p. 52° (no depression in mixed melting test). The products of the reaction were thus phenyl mercuric iodide, mercuric iodide, benzene and dibenzyl.

Photoreaction of dibenzyl mercury with iodobenzene in benzene. A solution comprising 1.2 g dibenzyl mercury, 0.6 g iodobenzene and 20 ml benzene was irradiated for about 50 hours. The precipitate was filtered off and found to weigh 0.7 g. There was isolated from it 0.6 g (60% of theory) of phenyl mercuric iodide with m.p. 273° (no depression in mixed melting test). The remaining 0.1 g was mercuric iodide. Benzene was distilled off from the filtrate. Steam distillation of the residue yielded an insignificant amount of crystals of dibenzyl, oxidation of which with permanganate gave benzoic acid with m.p. 121° (no depression in mixed melting test). The products of decomposition were therefore phenyl mercuric iodide, mercuric iodide and dibenzyl.

Photoreaction of diphenyl mercury with methyl iodide in methyl alcohol. A solution comprising 1.0 g diphenyl mercury, 0.8 g methyl iodide and 25 ml methyl alcohol was irradiated for about 50 hours in a test tube connected to a gas buret. 80 ml methane were evolved during the reaction, as shown by gas analysis. The precipitate was filtered off and found to weigh 0.95 g. Recrystallization

from ethylene dichloride gave 0.90 g (90% of theory) of phenyl mercuric iodide with m.p. 274 (no depression in mixed melting test). The methyl alcohol was distilled off from the filtrate, diluted with water and treated with carbon tetrachloride to remove the benzene. Nitration of the latter yielded a very small amount of m-dinitrobenzene with m.p. 89-90° (no depression in mixed melting test). Formaldehyde was found in the aqueous alcoholic solution by the silver mirror and resorcinol tests. The reaction products were therefore phenyl mercuric iodide, methane, benzene and formaldehyde.

Photoreaction of triphenylantimony with methyl iodide in methyl alcohol. A solution of 1.0 g triphenylantimony, 0.8 g methyl iodide and 25 ml methyl alcohol was irradiated for about 40 hours in a test tube connected to a gas buret. During the reaction 76 ml of methane was evolved, as established by gas analysis. The methyl alcohol was distilled off from the reaction mixture and formaldehyde was detected in it by the resorcinol test. After distillation of the solvent there was obtained 1.0 g (60% of theory) of triphenyl antimony diiodide which was converted into triphenylantimony dihydroxide with m.p. 199°. Therefore the reaction products were triphenylantimony diiodide, methane and formaldehyde.

Photoreaction of dibenzyl mercury with methyl iodide in methyl alcohol. A solution comprising 1.0 g dibenzyl mercury, 0.8 g methyl iodide and 25 ml methyl alcohol was irradiated for about 40 hours in a test tube connected to a gas buret. The reaction yielded 96 ml methane according to the gas analysis. The methyl alcohol was distilled off from the reaction products and formaldehyde was detected in it by the silver mirror test. The residue following distillation of the methyl alcohol was mixed with acetone and the acetone-soluble portion distilled in steam to give 0.3 g dibenzyl with m.p. 52°(no depression of m.p. of pure specimen). The acetone-insoluble portion was identified as mercuric iodide. The reaction products were therefore mercuric iodide, dibenzyl, methane, and formaldehyde.

Photoreaction of dibenzyl mercury with methyl iodide in benzene. A solution comprising 1.0 g dibenzyl mercury, 0.8 g methyl iodide and 25 ml benzene was irradiated for about 40 hours in a test tube connected to a gas buret. The reaction yielded 26 ml ethane according to the gas analysis. 0.5 g mercuric iodide (41% of theory) was filtered off. Benzene was distilled off from the residue. The residue following removal of the solvent was steam-distilled to give 0.2 g dibenzyl with m.p. 52° (no depression in mixed melting test). Accordingly the reaction products were mercuric iodide, dibenzyl and ethane.

Photoreaction of diethyl mercury with iodobenzene in methyl alcohol.[1] A solution comprising 4.2 g diethyl mercury, 3.7 g iodobenzene and 25 ml methyl alcohol was irradiated for about 30 hours in a test tube connected with a gas buret. The reaction yielded 353 ml gas, which was found by analysis to consist of 82.8% ethane and 17.1% ethylene. The residue in the test tube was filtered off and weighed. There was obtained 2.98 g ethyl mercuric iodide with m.p. 187° (no depression in mixed melting test). The distilled methyl alcohol was diluted with water and extracted with carbon tetrachloride to give benzene which was nitrated to form 0.8 g m-dinitrobenzene with m.p. 89-90° (no depression in mixed melting test). In the aqueous alcoholic solution formaldehyde was detected by the fuchsin-sulfur dioxide test, and a formaldehyde derivative with dimedone, m.p. 189°, was obtained. In addition 0.65 g metallic mercury was isolated. The reaction thus gave ethyl mercuric iodide, benzene, metallic mercury, ethane and ethylene.

[1] Student Z. Manchinova participated in this part of the investigation.

Photoreaction of dimethyl mercury with iodobenzene in methyl alcohol. A solution comprising 1.5 g dimethyl mercury, 1.2 g iodobenzene, and 25 ml methyl alcohol was irradiated for about 40 hours in a test tube connected to a gas buret. There was obtained 80 ml methane according to the gas analysis. The precipitate was filtered off and weighed. There was obtained 1.1 g (50% of theory) of methyl mercuric iodide with m.p. 144° (no depression in mixed melting test). The solvent was distilled off and diluted with water, and from the solution benzene was extracted with carbon tetrachloride. There was obtained 0.3 g m-dinitrobenzene with m.p. 89° (no depression in mixed melting test). Formaldehyde was detected in the aqueous alcoholic solution. Thus the products were methyl mercuric iodide, benzene, methane and formaldehyde.

Photoreaction of dimethyl mercury with iodobenzene in benzene. A solution comprising 1.5 g dimethyl mercury, 1.2 g iodobenzene and 25 ml benzene was irradiated for about 40 hours in a test tube connected to a gas buret. 78 ml gas was evolved and found to be ethane. 1.0 g methyl mercuric iodide with m.p. 144° (no depression in mixed melting test) was filtered off. After distilling off the solvent a small amount of diphenyl was isolated by steam distillation. Therefore the reaction products comprised methyl mercuric iodide, ethane and diphenyl.

Photoreaction of iodobenzene with metallic mercury in benzene. 1.83 g iodobenzene and 13 g metallic mercury in 10 ml benzene were irradiated for about 20 hours with agitation. The precipitate consisting of phenyl mercuric iodide and mercuric iodide was extracted with ethylene dichloride when 0.2 g phenyl mercuric iodide was isolated. M.p. 274° (no depression in mixed melting test). The yield of mercuric iodide was 0.4 g. The very same products were obtained in a similar experiment using methyl alcohol.

SUMMARY

1. The photochemical reactions of organomercury compounds with iodo derivatives in solution in benzene and methyl alcohol were investigated.

2. Dibenzyl mercury reacts with iodobenzene in methyl alcohol to form phenyl mercuric iodide, dibenzyl and benzene. The same substances in benzene solution give phenyl mercuric iodide, mercuric iodide, and dibenzyl.

3. Dimethyl mercury and methyl iodide in methyl alcohol react with formation of mercuric iodide, dibenzyl, methane and formaldehyde. The same components in benzene yield mercuric iodide, dibenzyl and ethane.

4. Diphenyl mercury and methyl iodide in methyl alcohol form phenyl mercuric iodide, methane, benzene and formaldehyde.

5. Dimethyl mercury with iodobenzene in methyl alcohol form methyl mercuric iodide, benzene, methane and formaldehyde. The same substances in benzene solution yield methyl mercuric iodide, ethane and diphenyl.

6. Diethyl mercury with iodobenzene in methyl alcohol react to form ethyl mercuric iodide, metallic mercury, ethane and ethylene.

7. Triphenylantimony with iodobenzene in methyl alcohol form triphenylantimony diiodide, benzene and formaldehyde. The same substances in benzene solution give triphenyl antimony diiodide and diphenyl; in chloroform they give triphenylantimony diiodide, benzene and hexachlorethane.

8. Triphenylantimony with methyl iodide in methyl alcohol yield triphenylantimony diiodide, benzene and methane.

9. A mechanism is proposed for all the above-described reactions, based on photolysis of the organoiodine compounds to atomic iodine and free radicals, and the subsequent behavior of the latter is investigated.

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2) See Consultants Bureau English translation, p. 1549.

REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

IX. REACTION OF DIAZOACETIC ESTER WITH ALLYL ALCOHOL IN PRESENCE OF COPPER

I. A. Dyakonov and student N. D. Pirogova

In a previous communication [1] one of us has shown that reaction of diazoacetic ester with allyl bromide in presence of copper powder leads to ethyl α-bromallyl acetate in a yield of 68-74% of theory:

$$CH_2=CHCH_2CHBrCOOC_2H_5. \qquad (I)$$

It appeared of interest to examine the possibility of extending this unusual reaction to other derivatives of olefinic hydrocarbons containing a double bond in the allyl position to the functional group, and in particular to unsaturated alcohols. In this investigation we have studied the action of ethyl diazoacetate upon allyl alcohol in presence of copper as catalyst. In analogy with the previous results the formation of the ester of α-hydroxyallyl-acetic acid was anticipated (II); it was also conjectured that the cyclic ester (III) might be formed and that an esterification reaction might take place, leading to the synthesis of the ethyl ester of allyl hydroxyacetic acid (IV). The second of these possibilities is the most widespread type of reactions of Class II with unsaturated compounds [2]. The esterification reaction was investigated by Curtius with reference to saturated alcohols of the aliphatic series in presence of sulfuric acid as catalyst [3].

$$CH_2=CHCH_2OH + N_2CHCOOC_2H_5 \xrightarrow{Cu} \begin{cases} CH_2=CHCH_2COHCOOC_2H_5 + N_2 \quad (1) \\ \quad (II) \\ CH\text{—}COOC_2H_5 \\ CH_2\text{—}CHCH_2OH + N_2 \quad (2) \\ \quad (III) \\ CH_2=CHCH_2OCH_2COOC_2H_5 + N_2. \quad (3) \\ \quad (IV) \end{cases}$$

A by-product that may be expected to be formed in this reaction is the ester of fumaric acid which is generally formed under these conditions by dimerization of diazoacetic ester radicals ($>CHCOOC_2H_5$) [4]. In reality it was only possible to detect two products of the reaction and to characterize them: the ethyl ester of allyl hydroxyacetic acid (IV) in a yield of 52.5% of theory, and the ethyl ester of trans-2-(ω-hydroxymethyl)-cyclopropane-1-carboxylic acid (III) in a yield of 7.2% of theory. The presence of ester (II) in the reaction products could not be confirmed in a single experiment. From the ratio of the yields of the two esters we can get a rough idea of the relative velocities of the two competing reactions (2) and (3). It is clear that the velocity of esterification is 7.5 times greater than the velocity of addition at the double bond of allyl alcohol.

Both the above-described esters (III) and (IV) were prepared by us for the first time. In order to demonstrate the structure of ester (IV), it was hydrolyzed in an alkaline medium to the corresponding allyl hydroxyacetic acid $CH_2=CHCH_2OCH_2COOH$ (V) in a yield of 74% of theory. The acid (V) has likewise not previously been described in the literature. Various cleavage methods were used for the purpose of establishing its structure; only those results obtained in the dealkylation reaction proved to be entirely satisfactory. Oxidation with potassium permanganate in a neutral medium did not lead to the desired objective.

objective: in place of the anticipated diglycolic acid, oxalic acid was found in the reaction products together with a small amount of formic acid. This result can evidently be expressed by the following equation:

$$(V) \xrightarrow[(KMnO_4)]{} [CH_2OHCHOHCH_2OCH_2COOH] \longrightarrow 2HOOCCOOH + (CO_2) + HCOOH, \quad (4)$$

or by further oxidation of the initially formed diglycolic acid according to the equation:

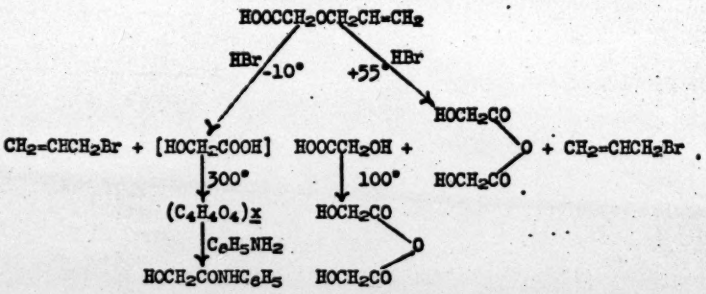
$$HOOCCH_2OCH_2COOH \xrightarrow[(KMnO_4)]{} 2(COOH)_2 . \quad (5)$$

Ozonization of acid (V) led to difficultly analyzable resin-like mixtures of acids of uncertain composition. Only the formation of formic acid was demonstrated. The consumption of ozone was 1½ times greater than had been expected on the basis of one double bond in allyl hydroxyacetic acid. Apparently under the ozonization conditions the ozone would be capable of cleaving the ether bond in the acid molecule, as observed by Fischer [5] in the case of ethers of the type of:

$$R_1CH_2OCH_2R_2 \xrightarrow{O_3} R_1COOCH_2R_2 + H_2O_2 . \quad (6)$$

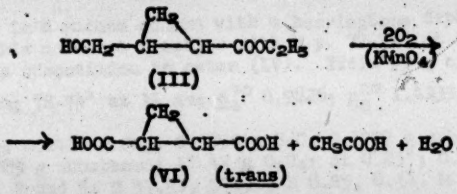
Simultaneous cleavage of the double bond and the ethereal bond of acid (V) would be expected to yield a difficultly analyzable mixture of acids of various structures as well as their corresponding half-aldehydes.

Dealkylation of acid (V) was effected by the method of saturation with dry hydrogen bromide followed by separation of the resultant reaction products. When performed at low temperatures (-10°) the reaction yielded as final products: allyl bromide (70.6% of theoretical yield) and a polyglycolide with the composition $(C_4H_4O_4)_x$ -- a product of transformation of the initially formed (under dealkylation conditions) glycolic acid (see Experimental). The polyglycolide was identified by conversion by the literature method into the anilide of glycolic acid [6, 7]. Performance of the dealkylation without external cooling led to formation of allyl bromide (69.6% yield), glycolic acid and its anhydride. The glycolic acid was not isolated in the pure (crystalline state). In order to confirm its formation, the crude product of the reaction was converted by prolonged heating into the anhydride of glycolic acid, using the method of Drechsel [8].



The data obtained are regarded as adequate evidence of the structure of allyl hydroxyacetic acid and in turn of the corresponding ester (IV).

The structure of the cyclic ether (III) was established by oxidation with potassium permanganate to trans-cyclopropane-1,2-dicarboxylic acid (VI):

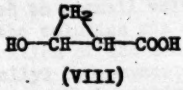


(III)

(VI) (trans)

The cis-form of acid (VI) was not isolated. In view of the high yield of the trans-form in the oxidation reaction (up to 80% of theory), it can be assumed that the trans-form also preponderates in the original ether (III). The small amounts of material at our disposal did not allow of closer investigation of this ether and the corresponding acid (VII). The latter is the nearest homolog of acid (VIII) which is apparently incapable of existence even in aqueous solutions of its salts [9]:

(VII)



(VIII)

In this connection the preparation of acid (VII) and the investigation of its properties are very desirable. It may be expected to be more stable than its lower homolog (VIII).

EXPERIMENTAL

1) Ethyl ester of allyl hydroxyacetic acid. In a flask fitted with a stirrer with a mercury seal, a condenser and a dropping funnel were placed 500 ml allyl alcohol (b.p. 96-97°, d_4^{20} 0.8541; n_D^{18} 1.4128) and 0.4 g copper powder. The alcohol was heated to boiling, and with energetic stirring a solution of 149 g crude diazoacetic ester in 120 ml allyl alcohol[1] was slowly introduced through the dropping funnel. The nitrogen evolved during the reaction was collected in a gasholder after flowing in turn through a condenser and a coil immersed in freezing mixture for separation of the alcohol vapor entrained by the gas. Evolution of nitrogen was observed immediately on introduction of diazoacetic ester into the flask, and it ceased as soon as the addition was completed.

The amount of nitrogen evolved was 23 l (18° and 735.5 mm), representing 83% of the theoretical amount. At the conclusion of the reaction the hot solution was filtered from catalyst and excess allyl alcohol distilled off in a vacuum of 100-110 mm. With external cooling of the receiver it was possible to recover up to 480 ml allyl alcohol. The product remaining in the distillation flask was distilled in vacuum (8 mm) and a fraction with a boiling range of 40-75° (8 mm) was collected. The residue from the distillation of this fraction was a viscous, resinous material with a dark color; it contained, as will be shown later, a small amount of cyclic hydroxy ester with a higher boiling point (see 4 below). The crude reaction product, b.p. 40-75 at 8 mm, was freed from admixed allyl alcohol and the higher boiling ether (III) by

[1] "Crude" diazoacetic ester is the preparation not purified by steam-distillation in vacuum. The yield of crude preparation according to our data, as well as to the literature data, is 80-85% of theory [10], that of the purified preparation is 60-65% of theory. Experiment revealed that the employment in this reaction of crude diazoacetic ester only caused a slight drop in the yield of ester of allyl hydroxyacetic acid in comparison with that obtained with the pure preparation.

fractional distillation in a vacuum column with a herringbone dephlegmator. There was isolated in this manner a fraction with b.p. 72-74° at 12 mm: n_D^{20} 1.4233, corresponding in composition to ester (IV). Yield 99 g or 52.5% of theory.

B.p. 66-68° at 8 mm; 72-74° at 12 mm; d_4^{20} 0.9826; n_D^{20} 1.4233; MR_D 37.350; Calc. 37.356.

0.1168 g substance: 0.2480 g CO_2; 0.0850 g H_2O; 0.1972 g substance: 0.4189 g CO_2; 0.1546 g H_2O; 0.1089 g substance; 17.47 g C_6H_6: Δt 0.23°; 0.2580 g substance: 17.47 g C_6H_6: Δt 0.50°. Found %: C 57.94, 57.90; H 8.25, 8.14. M 141.6, 141.2. $C_7H_{12}O_3$. Calculated %: C 58.29; H 8.40; M 144.1.

2) Allyl hydroxyacetic acid (V). 43.2 g (0.3 mole) of ester (IV) and 240 ml of 10% solution of potassium hydroxide in ethyl alcohol were boiled for 30 minutes under a reflux condenser, after which 2/3 of the original volume of alcohol was boiled off on the water bath. The residue in the distillation flask was neutralized with 10% sulfuric acid (phenolphthalein reaction) and then filtered from the precipitated inorganic salts. The filtrate was freed from residual alcohol by steam distillation and again concentrated to a small volume. After cooling and filtering again from inorganic salts, the solution was acidified with 50% sulfuric acid while being cooled. Acidification of the concentrated aqueous solutions is accompanied by separation of allyl hydroxyacetic acid (V) in the form of a yellowish oil above the water layer. When working with less concentrated solutions the acid (V) can be readily isolated with the help of ether extraction in a Soxhlet.

After drying of acid (V) in the ethereal solution with anhydrous sodium sulfate, the ether was driven off on the water bath, and acid (V) was distilled in vacuum. Yield of analytically pure preparation of acid (V) was 26.5 g or 74.2% of theory.

B.p. 108-109° at 7 mm; d_4^{20} 1.0965; n_D^{20} 1.440; MR_D 27.94; Calc. 27.90.

0.1591 g substance: 0.3022 g CO_2; 0.0979 g H_2O; 0.0972 g substance: 0.1845 g CO_2; 0.0599 g H_2O. Found %: C 51.80, 51.76; H 6.88, 6.89. $C_5H_8O_3$. Calculated %: C 51.72; H 6.94.

Determination of the equivalent of the acid (by direct titration using phenolphthalein as indicator). 0.1178 g substance: 9.78 ml 0.1 N NaOH; 0.1055 g substance: 8.78 ml 0.1 N NaOH; 0.1715 g substance: 14.25 ml 0.1 N NaOH. Found: equiv. 120.5, 120.1, 120.3 $(C_4H_7O)CO_2H$. Calculated: equiv. 116.1. Test for active hydrogen by the Terentev-Shcherbakova method gave a negative result.

The silver salt of the acid is unstable; it decomposes even in aqueous solution with separation of silver.

3) Oxidation of acid (V). 5.8 g (0.05 mole) of acid (V) was shaken at the ordinary temperature with 2% solution of potassium permanganate. Oxidation on the whole consumed 27.4 g (0.17 mole) of permanganate. After working up in the usual manner, the neutralized aqueous solution of oxidation products was tested for the presence of neutral, carbonyl-containing substances by distillation into an acetic acid solution of p-nitrophenylhydrazine. This test gave a negative result. The solution remaining in the distillation flask was then acidified with 50% sulfuric acid and subjected to steam-distillation for separation of the steam-volatile components from the non-volatile ones. The distillate was neutralized with caustic alkali (phenolphthalein test), then concentrated to a small volume and tested for formic acid by the calomel method. This test was positive. The acids non-volatile in steam were extracted with ether in a Soxhlet.

There was isolated from the ethereal extract the crystalline hydrate of oxalic acid with m.p. 102-104°. According to the literature the hydrate of

composition $C_2H_4O_2 \cdot 2H_2O$ melts at 101.5° [11]. A mixed melting test with an authentic specimen did not give a depression. After sublimation the acid melted at 188-189°, which was in accord with the literature data for the m.p. of anhydrous oxalic acid [11].

4) Ozonization of acid (V). Ozonization was performed on 4.17 g acid in solution in 40 ml dry chloroform. Quantitative determination of the amount of ozone consumed in cleavage of the above amount of acid (V) was effected by iodometric titration. The amount of ozone consumed was 2.7 g as against the theoretical requirement of 1.85 g for cleavage of one double bond. The duration of the ozonization was 11 hours. The ozonide was a colorless, viscous liquid insoluble in chloroform. After elimination of the chloroform, the ozonide was decomposed by boiling with water and the resultant aldehydes were oxidized by heating with hydrogen peroxide solution. The subsequent qualitative tests for the presence of aldehydes in the solution showed, however, that their removal during the preceding operation had not been complete.

The acids volatile in steam were separated from the non-volatiles by steam distillation. Substantial amounts of formic acid were detected in the distillate by the calomel method; 411.5 ml 0.1 N NaOH was required for neutralization of the acidic distillate as against the calculated amount of 404.3 ml 0.1 N NaOH. The solution remaining in the distillation flask, containing non-volatile acids, was evaporated to dryness in vacuum to give about 2 g of a brown liquid which turned black fairly rapidly and resinified when kept in a desiccator. It was impossible to purify and analyze the obtained acids.

5) Dealkylation of acid (V). Experiment 1. 17.4 g (0.15 mole) of allyl hydroxyacetic acid was placed in an Ivitsky bottle and saturated at -10° with dry, bromine-free hydrogen bromide. Absorption took place very energetically and saturation was effected very quickly. At the conclusion of the saturation the HBr gas was passed in for a further 20-30 minutes at -10°, and the two immiscible layers formed during the reaction were separated in a separating funnel. The upper layer was allyl bromide. The yield of crude product with b.p. 68-75° was 12.8 g (70.6% of theory). After fractionation the b.p. was 70-71°; d_4^{20} 1.402; n_D^{20} 1.469. Literature data: b.p. 71°; d_4^{20} 1.398; n_D^{20} 1.465 [12].

The lower layer was at first assumed to be bromacetic acid and was subjected to distillation in vacuum for purification. In spite of heating to 300° (8 mm) no product distilled over. On cooling, the whole of the material in the distillation flask solidified to a grey mass insoluble in the common organic solvents, soluble with difficulty in hot water, and readily soluble in hot aqueous caustic alkali. Recrystallization from nitrobenzene yielded a colorless powder with a m.p. 179°. The above properties and melting point are exhibited, according to Fahlberg [13][1] by the polyglycolide with the composition $(C_4H_4O_4)_x$, which is known to be formed together with other products when glycolic acid is heated to 240° [14]. The data now obtained therefore suggest that the final product of the dealkylation reaction was not bromacetic, but glycolic acid, and that the latter was converted into polyglycolide under the conditions of heating at a high temperature.

For final proof the latter was converted into glycolic acid anilide by heating with aniline to 130°, as recommended by Norton and Tschernjak [7]. After two crystallizations from water the anilide was obtained in the form of colorless platelets with m.p. 95-96°, in agreement with the literature [6].

[1] Other authors, however, give a higher m.p. for polyglycolide: 220° (Norton and Tschernjak [7] and 223° (Bischoff and Walden [6]).

0.1605 g substance: 13.5 ml N_2 (21°, 751.3 mm); 0.1464 g substance: 11.8 ml N_2 (20°, 763.2 mm). Found %: N 9.57, 9.41. $C_8H_{60}O_2N$. Calculated %: N 9.20.

Experiment 2. 34.8 g (0.3 mole) allyl hydroxyacetic acid was saturated with dry hydrogen bromide at first with cooling and later at room temperature. Passage of HBr without cooling led to fairly strong (50-60°) heating of the saturation bottle, following which the operation was suspended in order to avoid the risk of undesirable reactions. At the conclusion of the experiment the reaction product had separated into two layers just as in the previous one. The upper layer of allyl bromide weighed 25 g (69.6% of theory). When the lower layer was diluted with water a colorless powder separated out which was sparingly soluble in water and melted at 128-129°. The literature gives m.p. 128-130° for glycolic anhydride.

0.1348 g substance: 0.1788 g CO_2; 0.0511 g H_2O. Found %: C 36.17; H 4.24. $C_4H_6O_5$. Calculated %: C 35.83; H 4.51.

An attempt was made to isolate glycolic acid from the filtrate from the anhydride. For this purpose the solution following steam distillation was freed from hydrobromic acid and then concentrated in vacuum until a thick syrupy mass was obtained. It was impossible to isolate the contained glycolic acid in the crystalline form. The reason for the failure was that only perfectly pure glycolic acid will crystallize: even slight contamination with its anhydride, according to Drechsel [8], hinders the formation of crystals of glycolic acid.

It can easily be demonstrated that the syrupy mass contains traces of glycolic anhydride: on dilution with water (in a separate test) the anhydride (m.p. 128-129°) is at once precipitated. It is known that prolonged heating of glycolic acid on the water bath converts it into the anhydride (Drechsel [8]). In order to obtain confirmation of the presence of glycolic acid in the obtained syrupy product, the latter was also subjected to prolonged heating on the water bath. The experiment did indeed lead to the formation of the expected anhydride. M.p. 128-129°. Total yield of anhydride 4-5 g (20-25% of theory).

6) Ethyl ester of trans-2-(ω-hydroxymethyl)-cyclopropane-1-carboxylic acid (III). It has already been pointed out in 1) that after performing the condensation with diazoacetic ester and distillation of the crude product in vacuum, there remained in the distillation flask a small quantity of resinous dark liquid. Similar substances are normally always formed in syntheses with diazoacetic ester conducted over copper catalysts, and as a rule they are not amenable to distillation in vacuum. However, on subjecting the obtained residue to heating in a 6 mm vacuum we obtained 13.5 g of distillate with b.p. 109-115 at 6 mm (n_D^{20} 1.454), corresponding in composition to the cyclic ester (III). Yield 7.2% of theory. In subsequent distillations we were unable to isolate a fraction with a narrower boiling range, and measurements revealed that the refraction likewise remains unchanged throughout the whole period of heating (n_D^{20} 1.454). With larger quantities of material it would probably have been possible to obtain a preparation with a higher degree of purity; in our case the carbon content was 0.55% too high and that of hydroxyl 0.41% too low.

B.p. 113-119° at 7 mm; d_4^{20} 1.0764; n_D^{20} 1.454; MR_D 36.25; Calc. 35.50. The increment is therefore 0.75.[1]

0.1436 g substance: 0.3105 g CO_2; 0.1127 g H_2O; 0.0926 g substance: 0.1991 g CO_2; 0.0699 g H_2O; 0.1250 g substance; 16.29 g C_6H_6: Δt 0.26°; 0.0950 g substance; 17.31 g C_6H_6: Δt 0.19°. Found %: C 58.80, 58.90; H 8.42, 8.41. M 152.9, 149.2. $C_7H_{12}O_3$. Calculated %: C 58.38; H 8.40. M 144.1. 0.1005 g substance: 15.82 ml CH_4 (16.5°, 763.5 mm) (method of Terentyev-Shcherbakova) Found %: OH 11.39. $C_7H_{12}O_3$. Calculated %: OH 11.80.

[1] The literature reports an increment of 0.7 on the average for the trimethylene ring.

7) Oxidation of ester (III). 3.6 g (0.025 mole) ester (III), 15 ml 10% sodium hydroxide solution and the amount of potassium permanganate calculated from equation (7) (10.53 g = 0.066 mole) in the form of a 2% solution were placed in a thick-walled bottle which was tightly closed with a cork and then mechanically shaken at room temperature. After the lapse of two days the oxidation was complete (a slight excess of oxidizing agent was removed with sodium thiosulfate solution). The aqueous solution was filtered from manganese dioxide, the filtrate was concentrated on the water bath and acidified with sulfuric acid. The acetic acid formed by oxidation was distilled off with steam, while the residue in the distillation flask was extracted with ether in a Soxhlet for 12 hours. After drying the ether extract and driving off the ether, there was obtained 2.78 g (0.0214 mole) of crude trans-cyclopropane-1,2-dicarboxylic acid (VI) with m.p. 163°. Yield 83% of theory. A single crystallization from water raised the m.p. to 175°, and this did not change after repeated crystallizations. According to the literature this acid melts at 175°.

0.1326 g substance: 0.2240 g CO_2; 0.0556 g H_2O; 0.1173 g substance: 0.1993 g CO_2; 0.0494 g H_2O. Found %: C 46.08, 46.27; H 4.69, 4.71. $C_5H_6O_4$. Calculated %: C 46.19; H 4.65. 0.1171 g substance: 18.1 ml 0.1 N NaOH; 0.1785 g substance: 27.6 ml 0.1 N NaOH. Found: equiv. 64.7, 64.7. Calculated: equiv. 65.0.

SUMMARY

1. In a study of the reaction of diazoacetic ester with allyl alcohol in presence of copper, the ratio of the velocities of addition to the double bond of allyl alcohol and of its esterification by the diazoacetic ester was found to be 1 : 7.5.

2. It was established that the products of these reactions are the previously undescribed ethyl ester of allyl hydroxyacetic acid (IV) and the ethyl ester of trans-2-(ω-hydroxymethyl)-cyclopropane-1-carboxylic acid (III).

3. Alkaline hydrolysis of the ester (IV) gave the hitherto unknown allyl hydroxyacetic acid (V), the structure of which was established by oxidation, ozonization and dealkylation.

4. The structure of ester (III) was established by oxidation to trans-cyclopropane-1,2-dicarboxylic acid (VI).

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REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

X. INVESTIGATION OF THE REACTION OF DIPHENYLDIAZOMETHANE WITH ALLYL ALCOHOL

I. A. Dyakonov

In a previous communication [1] it was shown that in the reaction of ethyl diazoacetate with allyl alcohol in presence of copper powder, two main reaction products are formed: the ethyl ester of allyl hydroxyacetic acid and the ethyl ester of 2-hydroxy methylcyclopropane-1-carboxylic acid in the quantitative ratio of 1:1.

In the present paper, dealing with the reaction of diphenyldiazomethane with allyl alcohol, it is shown that the reaction between the two components is readily effected even in the absence of a catalyst[1] if the diphenyldiazomethane dissolved in allyl alcohol is added dropwise to a considerable excess of the alcohol heated to boiling. Just as in the case of ethyl diazoacetate two concurrent reactions are observed: etherification of the hydroxyl of the alcohol and addition of the diphenyldiazomethane radical $>C(C_6H_5)_2$ at the double bond of the alcohol. The products of this reaction--allylbenzhydryl ether (I) and 2,2'-diphenyl-1-hydroxymethylcyclopropane (diphenyl cyclopropyl carbinol) (II) -- are formed in the ratio of 3:2.

$(C_6H_5)_2CH-O-CH_2-CH=CH_2$ (I) $\qquad$ $(C_6H_5)_2C(CH_2)CH-CH_2OH$ (II).

The overall yield of the two isomers (I) and (II) in this reaction is 53.4% of the theoretical.[2] Secondary products of the reaction are tetraphenylazamethylene (ketazine) $(C_6H_5)_2C=N-N=C(C_6H_5)_2$ (yield 6-7% of theory calculated on the diphenyldiazomethane) and benzophenone, the yield of which was not taken into consideration (see below). Ketazine is formed by thermal decomposition of diphenyldiazomethane [3], and benzophenone by oxidation of diphenyldiazomethane by atmospheric oxygen during the reaction. A considerable amount of resinous products is also formed during the reaction.

The principal reaction products (I) and (II) were carefully investigated. The ether (I) had a constant boiling point and is characterized by other physical constants; it was separated by careful fractionation from the turbid, opaque first running containing the benzophenone. The latter forms a mixture with the ether which is not easily separated by distillation. Although the elementary analysis data were found satisfactory for the ether (I), the molecular weight in a series of determinations proved to be rather lower than the calculated value. This discrepancy was linked with the presence in the ether of traces of benzophenone, the composition of which is close to that of the ether but the molecular weight of which is much lower than that of the ether (see the details for analysis of the ether in the Experimental). This supposition was confirmed when the ether was investigated by the method of dealkylation with hydrogen bromide:

$$CH_2=CH-CH_2O-CH(C_6H_5)_2 + 2HBr \longrightarrow CH_2=CH-CH_2Br + (C_6H_5)_2CHBr. \quad (1)$$

[1] There is only one paper in the literature on the action of diphenyldiazomethane on alcohols of the aliphatic series, namely that of Staudinger and coworkers [2] in which it is reported that on heating diphenyldiazomethane in absolute alcoholic solution there is formed ethylbenzhydryl ether together with ketazine.

[2] The low yields of both compounds arise in course of their separation from the crude product and their purification (see Experimental).

Products isolated after dealkylation were allyl bromide (60% yield) and, instead of the crystalline diphenyldibromomethane (m.p. 45°), a liquid bromide with a bromine content lower than the theoretical. This was at first thought to be due to incomplete dealkylation and to consequent contamination of the final product with ether (I). It was therefore decided to vary not only the conditions of the dealkylation reaction (including treatment of the ether with gaseous hydrogen bromide and heating with hydrobromic acid in a sealed tube -- see Table 1, Experimental), but also to undertake repeated treatment of the already separated reaction products with hydrogen bromide or hydrobromic acid. As can be seen from the data in the Experimental part, the change in the method of treatment of the ether with HBr had little effect upon the constants of the obtained bromide, and it was impossible to effect the isolation of pure diphenylbromomethane in spite of repeated treatment of the crude bromide with hydrogen bromide (see expts. 1-5, Table 1). In one experiment only (see expt. 6) was a small amount of crystals of diphenylbromomethane obtained by careful rectification of the crude bromide followed by freezing of individual fractions. The material was identified by comparison with an authentic specimen. The non-crystallizing portion of the bromide also contained diphenylbromomethane in the dissolved form, since when heated with soda solution it gave the well-crystallizing and high-melting benzhydryl ether:

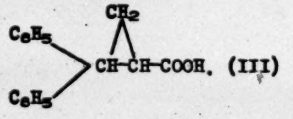
$$2(C_6H_5)_2CHBr + H_2O \longrightarrow (C_6H_5)_2CHOCH(C_6H_5)_2 + HBr. \quad (2)$$

In addition to the benzhydryl ether this reaction also yields a small amount of halogen-free oily material. Analysis of the latter showed it to be a mixture, but it was found possible to separate from it crystalline benzophenone (see experimental part).

Another possible component of this oil is benzhydrol (judging by the molecular weight of the material and the presence of active hydrogen -- see analysis). It could be formed as a secondary product of the reaction as represented by equation (2).

It can therefore be assumed that contamination with benzophenone of the diphenylbromomethane prepared by dealkylation was actually the cause of the difficulty of its separation in the pure form from the reaction products.[1] It is also perfectly clear that benzophenone could not be a product of the dealkylation reaction but was already present as an impurity in the original ether and was therefore a by-product of the condensation reaction itself.

The cyclic alcohol (II), isolated in the pure form by vacuum fractionation of the crude condensation product, is a highly viscous, yellowish oil, solidifying but not crystallizing below 0°. It should be mentioned that a considerable exaltation takes place in the molecular refraction (0.81) of alcohol (II) apparently due to conjugation of the three-membered ring with two phenyl radicals attached to one and the same carbon atom of the ring. In order to demonstrate the cyclic structure of the alcohol, the latter was oxidized with potassium permanganate in acetone solution to 2,2-diphenylcyclopropane-1-carboxylic acid (III):



[1] Authentic diphenylbromomethane was prepared by the action of HBr solution in glacial acetic acid under the dealkylation conditions of experiment 6 (see experimental part). After distillation in vacuum it immediately and completely crystallized.

The crystalline 3,5-dinitrobenzoate of the alcohol with m.p. 140° was also prepared. All the three compounds here described -- ether (I), alcohol (II) and acid (III) -- have not been reported in the literature.

The tertiary alcohol $(C_6H_5)_2C(OH)-CH\overset{CH_2}{\diagup\diagdown}CH_2$ described by Lipp [4] is an isomer of our alcohol (II). On treating his alcohol with anhydrous potassium bisulfate, Lipp obtained the ether $C_{32}H_{30}O$ instead of the expected hydrocarbon with a heptacyclic double bond, while by treatment with PBr_3 "under the usual conditions" he obtained a cyclic bromide $C_{16}H_{15}Br$ which was then converted into the corresponding iodide; the latter was used by the author as starting material for his experiments on the synthesis of the hydrocarbon $C_{16}H_{14}$.

We did not succeed in performing the reactions described by Lipp with primary diphenylcyclopropyl carbinol (II). An attempt to dehydrate the carbinol (II) with potassium bisulfate under the conditions indicated by Lipp for the isomeric tertiary alcohol led to formation of resinous polymers from which neither the crystalline ether $C_{32}H_{30}O$ nor the hydrocarbon $C_{16}H_{14}$ could be isolated. Exactly the same treatment of alcohol (II) with PBr_3 in absolute ethereal solution [9] using various ratios of reactants, and also in presence of pyridine [10], resulted mainly in resinous substances. Distillation of the crude reaction product in vacuum gave in some experiments a small quantity of distillate, analysis of which, however, gave results not consistent with the formula $C_{16}H_{15}Br$ (molecular weight and halogen content much below the calculated values). The product analyzed evidently was not an individual substance but a mixture of the original alcohol (or a product of its isomerization) with a monobromide of unknown structure.

EXPERIMENTAL[1]

1. Condensation of Diphenyldiazomethane with Allyl Alcohol

Diphenyldiazomethane was prepared by the previously described method [5]. Allyl alcohol was purified by rectification in a column. B.p. 96-97°; d_4^{20} 0.8541; n_D^{20} 1.413. Literature data: b.p. 97.06 (corr.); d_4^{20} 0.8540; n_D^{20} 1.41345 [6].

Into a flask equipped with a reflux condenser (ground-glass joint) and a dropping funnel was introduced 200 ml allyl alcohol, while a solution of 37 g diphenyldiazomethane in 40 ml allyl alcohol was placed in the dropping funnel. The condensation was effected by slow addition of the solution of diphenyldiazomethane to the allyl alcohol which was heated to boiling. At the close of the experiment the red color of the diphenyldiazomethane in the alcoholic solution had changed to pale yellow and did not change again in the course of further heating. Cessation of evolution of nitrogen from the reaction solution can also serve as a check on the completion of the reaction. Condensation of diphenyldiazomethane with allyl alcohol can also be effected by careful heating on a water bath of a highly diluted solution of diphenyldiazomethane in the alcohol.

Using the above method in several runs with 18-37 g diphenyldiazomethane in each, the amount of this reactant consumed was 91.4 g. At the completion of the reaction, the solutions obtained in the individual experiments were filtered if necessary from small amounts of ketazine, which usually separated when the solutions stood in the cold; the solutions were then combined and the allyl alcohol excess distilled off at 100 mm. The residual thick, yellow oil

[1] N. A. Lugovtsova and O. V. Guseva participated in the experimental work.

was transferred to a large vessel and diluted with approximately the 10- to 12-fold amount of cold ethyl alcohol. The alcoholic solution was allowed to stand in the cold for 1-2 days for crystallization of the main mass of ketazine which was difficultly soluble in cold alcohol. The total yield of ketazine was 6 g when starting from 91.4 g diphenyldiazomethane (about 7% of the theoretical yield). After two recrystallizations from hot alcohol or alcohol-benzene the m.p. was 161°. A mixed melting sample with authentic ketazine (m.p. 162°), obtained by the action of iodine on benzophenone hydrazone, melted at 161.5°.

The alcoholic solution remaining after filtration from the ketazine and containing the principal reaction product was freed from the alcohol by distillation, and the residue (a dark-colored oil) was fractionated in vacuum. In a first distillation the whole of the distillate came over in the range of 135-192° at 2-3 mm, with marked decomposition towards the end of the distillation. The viscosity of the distillate also increased steadily with rising temperature and its color in the higher boiling fractions was reddish-green. Only after repeated fractionations in a vacuum of 1-1.5 mm was it possible to isolate the following three fractions:

I. Opaque, dirty-white liquid with b.p. 105-130 (1.5 mm). Weight 3-4 g.

II. Nearly colorless, rather viscous oil with b.p. 130° (1.5 mm). Weight 37.8 g.

III. Highly viscous, yellow-colored oil with b.p. 160 (1.5 mm). Weight 23.0 g.

On seeding with a small crystal of benzophenone the first fraction began to crystallize while the mother liquor became transparent. After crystallization from alcohol the separated crystals melted at 48-49° and were identical with authentic benzophenone according to the mixed melting test. The first fraction is evidently a supersaturated solution of benzophenone in allylbenzhydryl ether (I) which in its turn consitutes the second fraction. The yield of ether (I) was 31.8% of theory (calculated on the diphenyldiazomethane). Fraction III is diphenylcyclopropyl carbinol (II) the yield of which in this reaction was 21.6% of the theoretical. A considerable quantity of viscous and higher boiling compounds of (I) and (II) is lost during fractionation of the crude condensation product in vacuum. In addition, however, to the ether and the alcohol, there is formed in the reaction a large amount of resinous polymers, judging by the residue in the distillation flask after the first vacuum distillation of the condensation product.

II. Allylbenzohydryl Ether (I)

The ether (I) is a colorless, transparent oil, less viscous than the cyclic alcohol (II). It turns yellow when stored.

B.p. 130° at 1.5 mm. 158-158.5° at 9 mm; d_4^{20} 1.053; $n_D^{20.3}$ 1.574; n_D^{25} 1.5702. Found: MR_D 70.23. $C_{16}H_{16}O$. Calculated: MR_D 70.06.

0.1582 g, 0.1666 g substance: 0.4975 g, 0.5234 g CO_2; 0.0953 g, 0.1037 g H_2O. 0.2063 g, 0.2585 g, 0.3719 g, 0.2018 g substance; 12.35 g, 17.05 g, 16.13 g, 17.27 g C_6H_6; Δt 0.410°, 0.375°, 0.570°, 0.295°. Found %: C 85.74, 85.70; H 6.74, 6.96; M 209.4, 207.9, 207.9, 206.6. $C_{16}H_{16}O$. Calculated %: C 85.69; H 7.18; M 224.3. $C_{13}H_{10}O$. Calculated %: C 85.67; H 5.40; M 182.2.

No active hydrogen was detected in the ether by the method of Terentyev Shcherbakova. The above-presented analytical data agree with those calculated for ether (I) with the empirical formula $C_{16}H_{16}O$ as well as with the calculated data for benzophenone ($C_{13}H_{10}O$). Four analyses are given for the molecular weight in view of the discrepancy between the experimental and calculated values

for ether (I). The causes of the discrepancy have been discussed above.

For the determination of its structure, the ether (I) was subjected to dealkylation with hydrogen bromide. Results of the various experiments on dealkylation of the ether carried out under different conditions are presented in the table. Reactions were effected: 1) By the action of a 47% aqueous solution of HBr, sometimes in presence of glacial acetic acid. 2) By the action of gaseous HBr. 3) By the action of gaseous HBr in glacial acetic acid. The temperature and duration of the experiments were also varied.

When using the first method (expt. 1) the largest possible quantity of 47% hydrobromic acid was added to the solution of the ether in glacial acetic acid consistent with the obtained solution still remaining transparent. Heating of the solution over a period of several hours under a reflux condenser led to deposition of a heavy, dark-colored bromide. Without separation of the layers, the solution was then distilled; the first portions of distillate were diluted with water for separation from the solution of the allyl bromide which was dried and redistilled. The residue in the distillation flask was also diluted with water, the solution neutralized with soda, and the bromide extracted with ether. After drying with $CaCl_2$ and driving off the ether, the residual oil was distilled in vacuum. The distillate is designated crude diphenylbromomethane in the table. In expts. 2 and 3 the crude diphenylbromomethane was subjected to repeated treatment with HBr.

In operation by the second method, the ether (I) was placed in an Ivitsky bottle which was externally cooled with a mixture of ice and salt; the ether was then saturated with dry hydrogen bromide prepared by the action of bromine on phosphorus in water. The hydrogen bromide was first freed from bromine by passage through a column containing anthracene supported on asbestos, and then through a column packed with phosphorus pentoxide on asbestos.

After completion of saturation, the mixture of bromides (emitting strong fumes of hydrogen bromide) was transferred to a Favorsky flask. The allyl bromide was distilled off first at the ordinary pressure; then under reduced pressure the crude diphenylbromomethane was distilled; the latter was subjected to a repeated vacuum fractionation in expt. 4. In one of the experiments (expt. 5) the mixture of bromides after saturation with hydrobromic acid was heated in a sealed tube for 10 hours at 40-60° in presence of hydrobromic acid.[1] The further treatment of the reaction products was the same as in expt. 4. In this experiment, in addition to allyl bromide there was formed a small amount of a second reaction product -- 1,3-dibromopropane.

In none of the above experiments was it possible to isolate diphenylbromomethane in the pure crystalline form (literature data [6]: m.p. 45°; b.p. 184° at 20 mm, 170° at 10 mm).

More satisfactory results were achieved in expt. 6. The crude bromide obtained in expt. 5 was subjected to heating in a sealed tube at 60-80° in a medium of glacial acetic acid saturated with gaseous HBr. After removing the solvent and distilling the residue in vacuum, three bromide fractions were obtained:

Fraction I: b.p. 152-153° (6 mm), 1.0 g. Fraction II: b.p. 153-154° (6 mm), 9.5 g. Fraction III: b.p. 154-156° (6 mm), 0.5 g. Fraction III crystallized in a freezing mixture. Partial crystallization of Fraction II was also possible by seeding. 4.8 g of nearly colorless crystals of diphenylbromomethane with

[1] Following Kizhner [7], who investigated the dealkylation of allyl ethyl ether by the action of hydrogen bromide.

Dealkylation of Ether (I)

	Ether (I) or crude diphenylbromomethane	Dealkylating agent and solvent	Experimental conditions (temp., duration, etc.	Crude diphenylbromomethane[2] b.p.	n_D^{20}	d_4^{20}	Yield (in % of theory)	Allyl bromide b.p.	n_D^{20}	d_4^{20}	Yield (in % of theory)
1	17.9	46 ml 47% HBr + 180 ml CH_3COOH	3-hours boiling under reflux condenser	135-143° at 2.5mm	1.616	–	61.3[2]	70-74°	1.462	1.402	60.5
2	12.0[1]	35 ml 47% HBr + 110 ml CH_3COOH	Same as in expt. 1; duration 1 hour	134-137° at 2.0mm	1.615	1.259	–	–	–	–	–
3	5.0[1]	50 ml 47% HBr	The same; in course of 6 hours	151-153° at 6 mm	1.615	1.257	–	–	–	–	–
4	16.1	HBr-gas	HBr passed through ether at -10°	155-158° at 7 mm	1.617	1.295	74.9[2]	69-72°	1.466	1.406	64.0
5	21.8	HBr-gas	Same as in expt. 4 but with subsequent heating in a sealed tube in presence of HBr at 60°; 10 hrs	152-156° at 6 mm	1.617	1.294	70.7[2]	70-73°	1.465	1.406	65.3
6	12.8[1]	CH_3COOH saturated with HBr gas	Heating in sealed tube at 60-80°; 2½ hours	152-155°[3] at 6mm	Partial crystallization of bromide		–	–	–	–	–

1) In Expt. 2 the starting material was not ether (I) but a crude reaction product of expt. 1 which we have arbitrarily called crude diphenylbromomethane. In expt. 3 the bromide recovered from expt. 2 was subjected to repeated treatment, while in expt. 6 the bromide from expt. 5 was used. (See text for explanation of this procedure.)

2) The yields of crude, noncrystallizing diphenylbromomethane are arbitrarily based on the pure preparation.

3) In expt. 6 the obtained crude diphenyldibromomethane partly crystallized; for this reason the constants and the percentage yield of the fraction with b.p. 152-156 (6 mm are not given here. (See text for further discussion.)

m.p. 37-39° was obtained by freezing and rapid filtration followed by washing of the crystals with petroleum ether. After crystallization from petroleum ether the diphenylbromomethane melted at 42-43° and did not depress the m.p. of an authentic specimen melting at the same temperature.

The non-crystallizing part of the bromide filtered off from the diphenylbromomethane in quantity of 5.8 g was subjected to boiling for 10 hours with dilute sodium carbonate solution. At the end of this period the solution was extracted with ether, the ether extracts dried with calcium chloride, and the solvent distilled off. The residue in the flask was a mixture of crystals and an oil. The oil was filtered at the pump from the crystals, and the latter after crystallization from alcohol weighed 0.9 g and melted at 108-109°.

Found %: C 88.96; H 6.61. $C_{26}H_{22}O$. Calculated %: C 89.13; H 6.33.

A mixed melting sample with benzhydryl ether (m.p. 108-109° compared with 110° reported in the literature [6]) prepared by the same method from authentic diphenylbromomethane did not exhibit any depression.

The light-yellow oil, filtered from the benzhydryl ether, was vacuum-distilled. Weight 1.3 g.

B.p. 148-150° (7 mm); d_4^{20} 1.104; n_D^{20} 1.603.

0.1397 g, 0.1182 g substance; 17.03 g, 15.76 g C_6H_6: Δt 0.240°, 0.227°; 0.1145 g, 0.1587 g substance: 4.9 ml, 6.45 ml CH_4 (17.5°, 756 mm). Found: M 177.1, 171.2; % OH 3.05, 2.90. $C_{13}H_{12}O$. Calculated: M 184, % OH 7.59. $C_{13}H_{10}O$. Calculated: M 182.

The values obtained agree with those calculated for benzhydrol. The molecular weight also agrees with that calculated for benzophenone. It follows from the above analytical data that the investigated substance cannot be homogeneous since the hydroxyl content found only represents at the most 40% of the calculated amount for a substance of similar molecular weight and containing only one hydroxyl group. The conclusion was reached that one of the components of the oil is benzophenone. On mixing the oil with an acetic acid solution of p-nitrophenylhydrazine a small quantity of crystals separated which on closer inspection proved to be not the p-nitrophenylhydrazone of benzophenone but benzophenone itself; m.p. 46°. A mixed melting test with authentic benzophenone did not give a depression (m.p. 48-49°).

III. Diphenylcyclopropyl Carbinol (II) and Diphenylcyclopropyl Carboxylic Acid (III)

The alcohol (II) is a yellow oil even more viscous than anhydrous glycerol. Below 0° it changes into a nearly solid, transparent mass but does not crystallize.

B.p. 160° at 1.5 mm;[1] d_4^{50} 1.072,[2] n_D^{50} 1.581; n_D^{25} 1.592. Found: MR_D 69.72. $C_{15}H_{16}O$. Calculated MR_D 68.91. Exaltation 0.81.

0.1752 g, 0.2144 g substance: 0.5539 g, 0.6751 g CO_2; 0.1163 g, 0.1378 g H_2O; 0.1872 g, 0.1172 g substance; 15.84 g, 19.06 g C_6H_6; Δt 0.270°, 0.140°; 0.1497 g, 0.1378 g substance: 16.1 ml, 14.9 ml CH_4 (19.5°, 749.4 mm). Found %: C 86.08, 85.88; H 7.43, 7.19; OH 7.53, 7.57; M 219.7, 227.2. $C_{16}H_{16}O$. Calculated %: C 85.69; H 7.18; OH 7.59; M 224.3.

1) On rapid distillation from a Favorsky flask with a broad dephlegmator. The most expedient method is to distil this alcohol from a Wurtz flask with a broad side tube sealed on low down.

2) It was impossible to determine the specific gravity at 20° owing to the high viscosity of the substance.

The 3,5-dinitrobenzoate, prepared from alcohol (II) by the usual method [8], melted at 140° after crystallization from a mixture of petroleum ether (b.p. 40-70°) and benzene (1 : 1). A second crystallization did not cause any change in melting point. From 1 g of alcohol (II) was obtained 1.35 g of the 3,5-dinitrobenzoate purified by crystallization (70% of the theoretical yield).

0.1031 g, 0.1031 g substance: 5.90 ml, 5.55 ml N_2 (19°, 763 mm). Found %: N 6.71, 6.41. $C_{23}H_{18}O_8N_2$. Calculated %: N 6.70.

Oxidation of alcohol (II) with potassium permanganate. 4.5 g (0.02 g-mole) of alcohol (II) was dissolved in 25 ml acetone, and to the solution at the ordinary temperature and with stirring was gradually added an acetone solution of 4.5 g of potassium permanganate. At first the oxidation proceeded fairly rapidly, but after half of the oxidizing agent had been added the process became very slow. In order to complete the reaction the remainder of the oxidizing agent was added to the solution at the boil (30 minutes). A small excess of permanganate which did not take part in the reaction was removed by adding 0.9 g sodium sulfite on cooling the solution. To the solution, which did not give an alkaline reaction with litmus, was then added a solution of 4 g potassium hydroxide in 50 ml water, and filtration from the manganese dioxide was effected; the latter was later also extracted with hot, weakly alkaline solution. The filtrate was combined with the alkaline extract and the combined solutions neutralized with dilute sulfuric acid. The neutral solution was distilled to eliminate the acetone and any steam-volatile substances that might be present. In the distillate were detected a small amount of oily liquid and white flocs of a substance which were not further examined owing to lack of material. The solution remaining in the distillation flask was concentrated to a volume of 75-100 ml, acidified with 10 ml of 70% sulfuric acid, and the resultant crust of crude acid was filtered off; there was obtained 1.6 g with m.p. 162-166°. The crude acid was dissolved in acetone, the solution diluted with water until turbid, then filtered and the filtrate concentrated. The crystals which separated when the solution cooled were purified by two crystallizations from benzene. M.p. 170-171°. Yield 1.05 g (22% of the theoretical).

0.1233 g, 0.1310 g substance: 0.3648 g, 0.3877 g CO_2; 0.0671 g, 0.0733 g H_2O; 0.2689 g, 0.2583 g substance: 11.6 ml, 11.1 ml 0.1 N NaOH (F 0.9852). Found %: C 80.71, 80.71; H 6.09, 6.26; equiv. 235.5, 236.2. $C_{15}H_{13}CO_2H$. Calculated %: C 80.59; H 5.92; equiv. 238.3.

The silver salt prepared from acid (III) was analyzed for its silver content:

0.2328 g, 0.1670 g substance: 0.0733 g, 0.0524 g Ag. Found %: Ag 31.49, 31.37. $C_{15}H_{13}O_2Ag$. Calculated %: Ag 31.30.

The silver salt of acid (III) is insoluble in water but fairly stable to light.

IV. Attempts to Prepare the Bromide $C_{15}H_{15}Br$ and to Dehydrate the Alcohol (II)

Action of PBr_3 on alcohol (II). 1) To a solution of 13.44 g (0.06 g-mole) of alcohol (II) in 50 ml absolute ether was added, not too slowly, a solution of 11.4 g (0.04 g-mole) of PBr_3 in 30 ml absolute ether. The reaction was exothermic and the ether reached the boiling point. The ethereal solution was then cooled and poured with stirring into a large volume of iced water; the ether layer was separated and washed with soda solution and water. After drying with $CaCl_2$ and distilling off the solvent, the residue was distilled in a 3-4 mm vacuum. The main reaction products were resinous polymers which remained in the distillation flask. A small quantity of brown distillate with b.p. 140-160° at 3-4 mm (with decomposition) was distilled again to give about 1-1.5 ml of a light-yellow oil

with b.p. 138-158° at 2mm; n_D^{17} 1.631.

0.1921 g substance: 0.0313 g AgBr. 0.1109 g, 0.1370 g substance: 17.96 g, 13.68 g C_6H_6: Δt 0.14°, 0.23°. Found %: Br 6.93; M 228.5, 223.2. $C_{16}H_{15}Br$. Calculated %: Br 27.64; M 287.3.

2) The bromination conditions were the same as in expt. 1 but the PBr_3 was used in an excess not exceeding 10% of theory. At the conclusion of the reaction the solution was left for 24 hours at room temperature and then treated with a cold 25% solution of potassium hydroxide. After washing the ether layer with water, drying, and distilling off the solvent, the residue was distilled in vacuum. Distillation was accompanied by decomposition and a large amount of resin was left in the flask. The dark-colored distillate was subjected to repeated rectification. From 28.9 g cyclic alcohol and 12.7 g PBr_3 was obtained, apart from resins, 3.8 g of distillate with b.p. 102-106° (0.5 mm) and 3.5 g distillate with b.p. 128-133° (0.5 mm):

First fraction with b.p. 102-106° (0.5 mm); n_D^{20} 1.6340; d_4^{20} 1.046.

0.2781 g substance; 16.81 g C_6H_6: Δt 0.377°. 0.1162 g, 0.1049 g substance: 0.0105 g, 0.0060 g AgBr. Found %: Br 3.05, 2.44; M 224.9. $C_{16}H_{15}Br$. Calculated %: Br 27.64; M 287.3.

Second fraction with b.p. 128-133° (0.5 mm); n_D^{20} 1.6279; d_4^{20} 1.088.

0.3078 g, 0.2755 g substance; 15.57 g, 16.85 g C_6H_6; Δt 0.40°, 0.35°, 0.1598 g substance: 0.0323 g AgBr. Found %: Br 8.60; M 257.0, 248.3. $C_{16}H_{15}Br$. Calculated %: Br 27.64; M 287.3.

Both fractions become very brown when kept, evidently due to decomposition.

3) Attempt to brominate alcohol (II) in presence of pyridine led to formation of a still greater quantity of resin: From 11.2 g alcohol, 13 g PBr_3 and 12 ml pyridine in ether solution was obtained only 0.8 g liquid distillate with an indefinite boiling temperature.

Action of potassium bisulfate on alcohol (II). 5.1 g cyclic alcohol (II) and 10 g anhydrous $KHSO_4$ were heated for 1.5 hours at 180° on an oil bath. The dark mass which solidified on cooling was treated with water and extracted with hot benzene. The benzene extract was dried with anhydrous potassium carbonate and the solution evaporated to dryness, leaving a residue of dark, viscous resin, soluble with difficulty in alcohol and readily soluble in benzene. It could not be distilled in vacuum, nor could any crystalline compounds be isolated from it by treatment with various solvents.

SUMMARY

1. On effecting reaction between diphenyldiazomethane and allyl alcohol there were obtained the previously unknown allyl benzhydryl ether and 2,2-diphenyl-1-(hydroxymethyl)-cyclopropane in the ratio of 3 : 2 at a total yield of 53.4% of the theoretical, together with by-products of the reaction (benzophenone and tetraphenylazamethylene.

2. A study was made of the dealkylation of allyl benzhydryl ether with hydrogen bromide, when it was shown that the ether contains a little benzophenone as impurity.

3. Oxidation of 2,2-diphenyl-1-(hydroxymethyl)-cyclopropane gave 2,2-diphenylcyclopropane-1-carboxylic acid, not previously described in the literature. An attempt to dehydrate the cyclic alcohol and to prepare its bromide by the action of phosphorus tribromide was not attended with success.

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REACTIONS OF KETENE DIMER

REACTION OF KETENE DIMER WITH SOME WEAKLY BASIC AROMATIC AMINES

V. V. Perekalin and O. M. Lerner

In recent years the attention of Russian chemists has been turned in ever increasing measure to ketene dimer, a highly reactive compound discovered more than 40 years ago [1] and undeservedly forgotten for a decade. Opinion as to the structure of ketene dimer is still not unanimous in spite of the many investigations of the problem [2], mainly of a physicochemical character (dipole moments, infrared absorption spectra, heats of formation and parachor). It may be regarded as definitely established, however, that ketene dimer is not a mixture of tautomers but a single substance [2]; the structure can probably be represented by the formula $CH_3-\underset{\underset{O}{\|}}{C}-CH=C=O$. Of the diverse reactions of ketene dimer, particular attention has been given to its interaction with various, chiefly primary, aromatic amines [3] with the objective of preparing arylides of acetoacetic acid by a simple and cheap method [4].

We have investigated the not previously studied reaction of ketene dimer with some weakly basic primary and secondary aromatic amines: diphenylamine, $K_{diss} = 5.6 \times 10^{-4}$ [5], o-nitroaniline, $K_{diss} = 5.6 \times 10^{-5}$ [6], and carbazole.[2] In spite of wide variation in the reaction conditions, it was only after using pyridine as a catalyst in acetone solution that the acetoacetyl derivative of diphenylamine (I) could be obtained in a yield of 70%. The catalytic action of pyridine is probably associated with the formation of a pyridine-diketene complex which decomposes to give activated molecules of diketene:

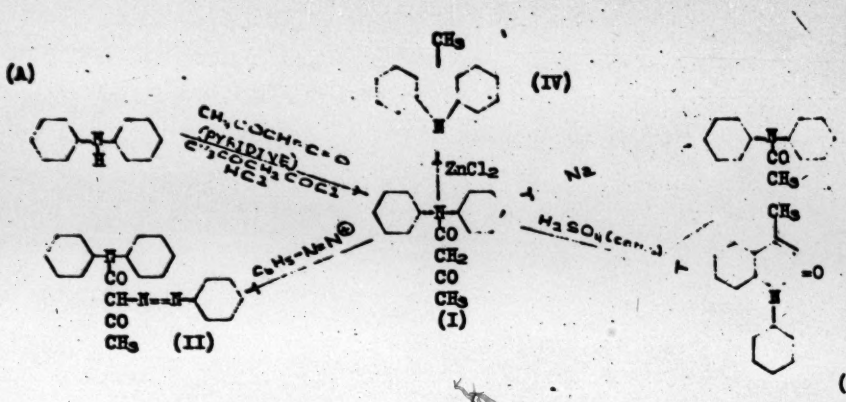
$$CH_3COCH=C=O + C_5H_5N \longrightarrow CH_3\overset{-}{C}OCH-\overset{+}{N}C_5H_5 \longrightarrow CH_3\overset{-}{C}OCH-\overset{+}{C}=O + C_5H_5N.$$

The little investigated acetoacetyl chloride [7] was used, without special success in the present case, as an acetylating medium, in addition to ketene dimer itself. The structure of the acetylated product was confirmed by its identity with acetoacetyldiphenylamine [8] synthesized by the method of amide condensation; it was also confirmed by its hydrolysis in an acid medium when the original diphenylamine was regenerated. The azo dye (II) and the lepidone derivative (III) of acetoacetyl diphenylamine, prepared from ketene dimer and acetodiphenylamine, appeared identical. An attempt to prepare acetonyl acridine from (I) by heating with anhydrous zinc chloride was not attended with success, meso-methylacridine (IV) being formed: [see (A) on following page].

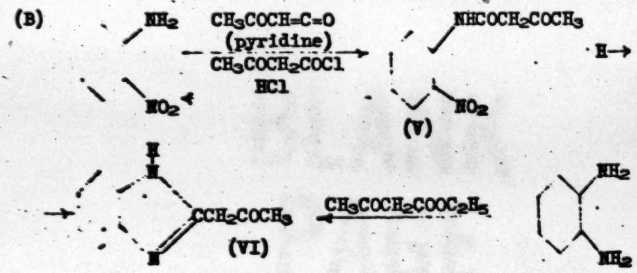
The reaction of ketene dimer with o-nitroaniline was performed with good yield also in presence of pyridine in an acetone medium. Reduction of o-nitroacetoacetanilide (V) gave acetonyl benzimidazole (VI), which proved to be identical with the imidazole obtained from o-phenylenediamine and ethylacetoacetate [9]. Reaction of o-nitroanilinewith acetoacetyl chloride took place, as in the case of diphenylamine, with low yields [see (B) on following page].

[1] See this reference in the literature cited.

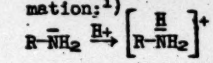
[2] We could not find the dissociation constant of carbazole in the literature; the ability to substitute metal for the hydrogen of the amino group is indicative not of the basic but rather of the acidic properties of carbazole.



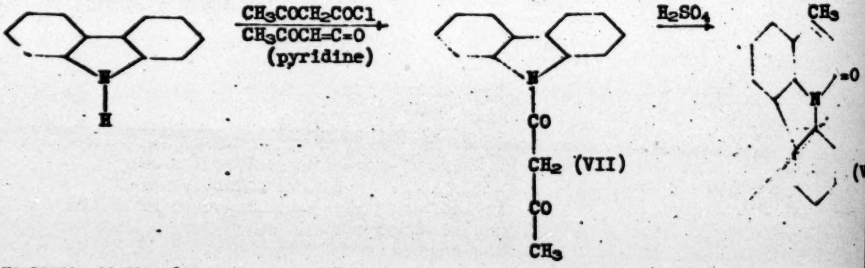
(III)



The difficulty of acylation of diphenylamine and o-nitro aniline with acetoacetyl chloride is apparently due to blocking of the unshared electron pair of the amino group by a hydrogen ion in consequence of salt formation;[1]



Since carbazole is an amphoteric amine, in presence of pyridine it reacted with difficulty with ketene dimer due to the poor activity of the unshared electron pair of the amino group. Owing, however, to the acidic properties of the hydrogen of the amino group, it readily entered into reaction with acetoacetyl chloride, forming acetoacetyl carbazole (VII), from which was prepared the lepidone derivative (VIII).



[1] The reaction does not take place in the cold, and it was effected at room temperature; it was accompanied by decomposition of the acid chloride into ketene dimer and hydrochloric acid.

Comparative data for yields of acetoacetyl derivatives are given below.

Table of Yields of Acetoacetyl Derivatives
(in % of theory)

Amine	Acylated substance		
	$CH_3COCH{=}C{=}O$	CH_3COCH_2COCl	$CH_3COCH_2COOC_2H_5$
Diphenylamine . .	64	10	Prepared by the method of amino condensation [8] 37
o-Nitroaniline ..	60	10	19
Carbazole	12	70	Not described

EXPERIMENTAL

1. Preparation of acetoacetyl chloride from ketene dimer and hydrogen chloride [10]. 8.1 g ketene dimer (0.1 mole) was placed in a reaction vessel equipped with stirrer and calcium chloride tube, cooled to -5° in a bath containing a mixture of kerosene and solid carbon dioxide, and saturated with dry hydrogen chloride, In the course of 10 minutes the temperature was then carefully reduced to -30°, taking care that ketene dimer should remain liquid.[1] As soon as the increase in weight of the ketene dimer exceeded the theoretical increase by 1-2 g, the saturation was stopped. Air was aspirated for 10-15 minutes through the layer of chloride for removal of the excess of hydrogen chloride at the same temperature and at a residual pressure of 20 mm. The acetoacetyl chloride (containing 0.5-0.01% excess hydrogen chloride) is an oily liquid fuming in the air and solidifying at -48°. At low temperature (-60-70°) the chloride did not undergo any change during 20 days.

2. Preparation of acetoacetyldiphenylamine from diphenylamine and ketene dimer in presence of pyridine. 16.9 g (0.1 mole) diphenylamine was dissolved in 60 ml acetone and cooled to -20° by addition of a small amount of solid carbon dioxide. Successive addition was then made to the solution of 0.5 ml pyridine and 2.7 g ketene dimer (0.15 mole). Over a period of 10 minutes the mixture was heated to boiling and was boiled for 45 minutes on the water bath under a reflux condenser (conclusion of the reaction was signalized by the disappearance of the odor of ketene dimer). At this stage the acetone was distilled off from the brown solution. Two methods of separation: a) The residual brown oil was dissolved at 40-50° in 1000ml 2% sodium hydroxide. The alkaline solution of the sodium salt of acetoacetyl diphenylamine was separated by filtration from the small resinous precipitate and acidified with 5% hydrochloric acid until a permanent cloudiness appeared. The free acetoacetyl derivative was then isolated with the aid of a stream of carbon dioxide. Yield 15 g (60% of the theoretical). Acetoacetyl diphenylamine is a colorless crystalline powder with m.p. 83-84° (from aqueous methyl alcohol); b) The crude acetoacetyl diphenylamine remaining after evaporation of the acetone was extracted twice in the cold with ether. Yield 16 g (64% of the theoretical). M. p. 83-84°.

[1] Ketene dimer can be quickly cooled to -30° without danger of freezing if 20-30% of toluene or xylene is first added.

3. Preparation of acetoacetyl diphenylamine (I) from diphenylamine and acetoacetyl chloride. To a solution of 8.5 g (0.05 mole) diphenylamine in 40 ml benzene cooled to -20° was added over a period of 10 minutes 8.5 g (0.075 mole) of acetoacetyl chloride which had been carefully freed from excess of hydrogen chloride.[1] The reaction mass was then heated for an hour at 40-50°. The reaction was considered at an end when no more hydrogen chloride came off. The brown-colored residue after evaporation of the benzene was dissolved in 2% sodium hydroxide at a temperature of 50-60°. The solution was freed from fused diphenylamine by decantation, after which a current of carbon dioxide was passed through and the free acetoacetyl diphenylamine was isolated. M.p. 78-80°. Yield 3 g (12% of the theoretical).

4. Preparation of acetoacetyl diphenylamine (I) by the method of amide condensation. The synthesis was effected by the literature method [8]. The product melted at 83-84°[2] (from aqueous methyl alcohol).

5. Hydrolysis of acetoacetyl diphenylamine. 2 g acetoacetyl diphenylamine was boiled for an hour with 50 ml 10% hydrochloric acid. The separated precipitate was filtered off, washed with dilute alkali and then with water and dried. M.p. 52°. A mixed melting sample with diphenylamine did not show any depression.

6. Preparation of N-phenyl lepidone (III) from acetoacetyl diphenylamine. 5 g acetoacetyl diphenylamine was dissolved in 50 ml sulfuric acid (specific gravity 1 84). On the following day the brown solution was poured into finely crushed ice. The resultant yellowish-green precipitate was filtered off and carefully washed with water. Quantitative yield of 4.5 g. Crystallization from aqueous acetone gave a nearly white crystalline product with m.p. 133-134°.

7. Preparation of the azo dye (II) from acetoacetyl diphenylamine. 2.53 g acetoacetyl diphenylamine was dissolved in 8 ml 0.1 N sodium hydroxide solution, diluted to 300 ml with water, and coupled for an hour with 100 ml 0.1 N solution of diazobenzene. With progressive addition of the diazobenzene the dye was precipitated; it was reprecipitated from dilute alkali. Finely crystalline brownish-red powder, m.p. 209° (from alcohol).

8. Preparation of o-nitroacetoacetanilide (V) from ketene dimer in presence of pyridine. 19.7 g (0.15 mole) o-nitroaniline was dissolved at room temperature in 50 ml acetone. To the brown solution was added a small amount of solid carbon dioxide in order to lower the temperature to -20°, followed in succession by 2 ml pyridine and 16.8 g (0.2 mole) ketene dimer. The frozen mixture was brought to the boil in the course of 10 minutes on the water bath and then boiled for 30 minutes (the end of the reaction was signalized by the disappearance of the ketene dimer odor), following which the acetone was distilled off and the residual brown oil treated with 300 ml 5% sodium hydroxide at 50-60°. The dark-brown solution was separated by filtration from the small amount of resin which did not dissolve in alkali, acidified with 5% hydrochloric acid until the cloudiness was permanent, and then subjected to a stream of carbon dioxide. After 30 minutes a yellowish-red precipitate came down which was insoluble in alcohol and acetone (yield about 10 g). More prolonged treatment with carbon dioxide (3 hours) gave a bright yellow crystalline precipitate of the acetoacetyl derivative which was filtered off, washed with ether and dried. Yield 19 g (60% of the theoretical). o-Nitroacetoacetanilide forms yellow, acicular crystals. M.p. 65° (from aqueous alcohol) in agreement with the literature [9].

[1] During the addition of the acetoacetyl chloride the hydrochloride of diphenylamine is precipitated.

[2] Repeated crystallization from various solvents failed to give a product with a higher melting point.

9. Preparation of o-nitroacetoacetanilide from o-nitroaniline and acetoacetyl chloride. To a solution of 13.8 g (0.1 mole) o-nitroaniline in 50 ml acetone at 15° was gradually added 12 g (0.1 mole) acetoacetyl chloride which had been carefully purified from excess hydrogen chloride. The mixture was then gradually heated over a period of 30 minutes on a water bath until the energetic evolution of hydrochloric acid had ceased. The acetone was evaporated off from the brown solution, the residue dissolved in 5% sodium hydroxide solution and the product filtered from the unreacted o-nitroaniline.

o-Nitroacetoacetanilide was isolated by passing a stream of carbon dioxide through the alkaline solution. Yield 2.2 g (10% of the theoretical), m.p. 65° (from aqueous alcohol). The amount of o-nitroaniline recovered was 12 g (86% of the original amount). At lower reaction temperatures the yields were even lower.

10. Hydrolysis of o-nitroacetoacetanilide. 2.2 g o-nitroacetoacetanilide was boiled for 2 hours with 50 ml 10% sulfuric acid. The o-nitroaniline which separated after cooling of the solution was filtered off, washed with water and dried. Yield 1.35 (quantitative). M. p. 70°. No depression in mixed melting test with authentic o-nitroaniline (m. p. 72°).

11. Preparation of 2-acetonyl benzimidazole (VI) by reduction of o-nitroacetoacetanilide. To a solution of 5 g o-nitroacetoacetanilide in 25 ml ethyl alcohol were added 3 ml of 4% hydrochloric acid and 8g iron filings. The reduction was considered complete after refluxing for 2 hours on a water bath. The deep-red solution was filtered from the iron oxide and unreacted iron, evaporated to one-third of the original bulk, and after cooling diluted with water. The light-yellow precipitate was filtered off and crystallized from water. M. p. 145°. The melting point was not depressed in admixture with pure 2-acetonyl benzimidazole prepared from ethylacetoacetate and o-phenylenediamine [9].

12. Preparation of N-acetoacetyl carbazole (VIII) from carbazole and acetoacetyl chloride. Acetoacetyl chloride was prepared from 15 g (0.18 mole) ketene dimer dissolved in 50 ml acetone, and dry hydrogen chloride. Removal of the excess of hydrogen chloride was not effected because it had no influence upon the course of the reaction. 20 g (0.12 mole) carbazole was added at -50° in the course of 10 minutes to the acetone solution of acetoacetyl chloride. The reaction set in at once, the carbazole went into solution and hydrogen chloride was evolved. After an hour the reaction vessel was taken out of the cooling bath, and after cessation of the vigorous evolution of hydrogen chloride (approximately after 2 hours) the reaction was considered at an end. The brown viscous mass was poured into a dish and the acetone evaporated off.

Isolation and purification. a) The reaction mass was dissolved at 50-60° in 1.5l of 2% sodium hydroxide. The solution was separated by filtration from unreacted carbazole (5 g = 25% of the original amount), and acidified with 5% hydrochloric acid until permanently cloudy; further precipitation was effected with carbon dioxide when a bright crystalline precipitate was formed. The latter was filtered off, washed with water and dried. Yield 19 g (63% of the theoretical). M. p. of N-acetoacetyl carbazole 118° (from aqueous acetone). b) The reaction mass was triturated with ether, the ether filtered off and the precipitate repeatedly washed with ether. The resultant N-acetoacetyl carbazole melted at 115-117°. Yield 21 g (70% of the theoretical).[1]

Analytical data for N-acetoacetyl carbazole are given below:
0.1421 g substance: 0.400 g CO_2; 0.0674 g H_2O; 0.1301 g Subst.: 0.3656 g

1) 3 g carbazole (15% of the original amount) was recovered from the ether extracts.

CO_2; 0.0676 g H_2O; 0.1546 g subst.: 7.4 m. N_2 (21°, 760 ml).
Found %: C 76.81, 76.69; H 5.3, 5.8; N 5.55. $C_{14}H_{13}O_2N$. Calculated %: C 76.47; H 5.2; N 5.57.

13. Preparation of N-acetoacetyl carbazole from ketene dimer and carbazole in presence of pyridine. 10 g (0.06 mole) carbazole was dissolved in a mixture of 40 ml benzene and 15 ml toluene. After cooling the solution to -20° with the aid of a small quantity of solid carbon dioxide, addition was made in succession of 6 g (0.07 mole) ketene dimer and 1 ml pyridine. The mixture was brought to the boil and boiled for 1.5 hours on the water bath under a reflux condenser. Disappearance of the odor of ketene dimer was considered to mark the end of the reaction. The solvent was evaporated from the brown solution; the N-acetoacetyl carbazole was purified by reprecipitation of the sodium salt followed by crystallization from aqueous acetone. M. p. 118°; yield 1.5 g (10%).

14. Preparation of 1,8-o-phenylene lepidone (VIII) from N-acetoacetyl carbazole.

A solution of 5 g N-acetoacetyl carbazole in 50 ml sulfuric acid (specific gravity 1.84) was left at room temperature for 24 hours. On pouring the sulfuric acid solution into a mixture of finely pounded ice and water, a greenish-grey precipitate of 1,8-o-phenylene lepidone came down and was carefully washed with water. Yield 4,5 g (quantitative). Crystallization from aqueous acetone gave 1,8-o-phenylene lepidone with m.p. 156-157°.

0.1159 g substance: 6.2 ml N_2 (21°, 760 mm). Found %: N 6.21. $C_{14}H_{11}ON$. Calculated %: N 6.00.

SUMMARY

1. It has been shown for the first time that ketene dimer can be successfully used for the preparation of acetoacetyl derivatives of weakly basic aromatic amines (o-nitroaniline, diphenylamine, carbazole, etc).

2. The acetoacetyl derivatives of o-nitroaniline and diphenylamine were obtained in much better yields than by earlier syntheses.

3. The possibility of utilizing acetoacetyl derivatives of weakly basic amines as azotols and for the preparation of complex derivatives of lepidone is demonstrated.

4. It is shown that acetoacetyl chloride may be used for acylating amines possessing amphoteric properties (e.g. carbazole, etc).

5. A mechanism for the activating action of pyridine on ketene dimer is proposed.

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THE SYNTHESIS OF METHYLCYCLOPROPYL CARBINOL

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At the present time derivatives of cyclopropane are of both theoretical and practical interest as starting materials for a series of compounds of potential value in industry and medicine. Great interest would therefore be attached to the development of a method for synthesis of methylcyclopropyl carbinol, a starting material for the synthesis of a series of monosubstituted derivatives of cyclopropane. Up to the start of our investigation the literature did not describe any good methods for preparation of this carbinol which could give a product of adequate purity in high yield.

Methylcyclopropyl carbinol was prepared for the first time by Demyanov and Pinegin [1] by reduction of methylcyclopropyl ketone with sodium in absolute alcohol. The carbinol yield was 50% of theory. The very same method was used by Michiels [2]. Although the yields are satisfactory, this method has the disadvantage of giving a byproduct in the form of a small amount of a carbinol with an open chain. Fractionation of this mixture does not always permit the isolation of the required product in a sufficiently pure form.

Henry [3] prepared methylcyclopropyl carbinol by the action of isobutyl magnesium bromide on methylcyclopropyl ketone. The secondary alcohol was then contaminated with methylisobutylcyclopropyl carbinol. For the purpose of isolating the secondary alcohol, the reaction products were converted into their acetates which were separated and saponified.

In the present investigation we reduced methylcyclopropyl ketone to methylcyclopropyl carbinol with aluminum isopropylate [4], [5].

Some slight modifications which we introduced into the method of working up of the reaction products enabled us to obtain a final product in a yield of 87% of theory. As can be seen from the combination scattering spectra detailed below, our methylcyclopropyl carbinol consisted of a single substance. There is no doubt that when using large quantities of the ketone the yield of carbinol could be increased to almost the theoretical value.

When our investigation had been completed two papers were published on the synthesis of the same methylcyclopropyl carbinol. In the first paper [6] the authors tried out three different methods of reduction of methylcyclopropyl ketone. The first was reduction with lithium aluminium hydride and gave good yields of carbinol (76% of theory) in a sufficiently pure state, but (as the authors point out) the synthesis of large quantities would involve great difficulties. Raney nickel was used in the second method but proved unsatisfactory since it gave a mixture of three products: the original ketone, methylcyclopropyl carbinol and pentanol-2. Barium-promoted copper-chromium catalyst was used in the third method. Yields of carbinol reached 90%, but the product was also contaminated with pentanol-2.

In the second of these papers 4 methods are described, of which the best results were given by reduction of the ketone with lithium aluminium hydride. Hydrogenation over nickel-on-kieselguhr at high pressure and 50-60° led to the formation of very large amounts of an open-chain compound, while reduction with sodium in liquid ammonia led to complete rupture of the three-membered ring. The fourth of these methods is the same as ours, but in the authors' modification it gave very low yields of carbinol (23% of theory) and a large amount of condensation products.

Table 1 gives the properties of methylcyclopropyl carbinol prepared by various methods.

Table 1

Authors	B. p.	d_4^{20}	n_D^{20}	Method of Synthesis
Demyanov and Pinegin [1]	122.5°	0.8856	1.4285	Na in absolute alcohol
Michiels [2]	119—120	0.8804	1.42461	Na in absolute alcohol
Henry [3]	123—124	0.88778	1.42966	Grignard synthesis
Demyanov and Pinegin [15]	122.4—122.9	0.888	1.431	From cyclopropyl ethylamine
Present investigation. . .	122.4—122.6	0.8885	1.43140	With aluminium isopropylate
Slabey and Wise [6]	122.51	0.88860	1.43160	With Cu—Cr catalyst
Volkenburg and others [7] .	123.5	0.8893	1.4316	With Li—Al hydride

We see from Table 2, which details the combination scattering spectra obtained by us for the carbinol and the ketone and also gives the spectra of cyclopropane, ethylcyclopropyl ketone and cyclopropyl carbinol, that our product is a homogeneous carbinol of the cyclopropane series. The value of the frequency of the carbonyl bond in methylcyclopropyl ketone is somewhat lower than that of the carbonyl in ethylcyclopropyl ketone (1695 and 1701 cm^{-1} respectively). This is paralleled by the case of acetone and methylethyl ketone (1707 and 1711 cm^{-1} respectively). The frequencies of the carbonyl in the cyclopropane series are lower than in the structurally similar ketones of the aliphatic series. Thus for methylisopropyl ketone it is equal to 1709 cm^{-1}. We ascribe this depression to pseudoconjugation which indicates that the cyclopropane ring possesses the properties of a double linkage to a certain degree. In the case of true conjugation, as for instance in ethylidene acetone, this value for the carbonyl frequency is still lower and equal to 1685 cm^{-1} [8].

Table 2

Combination Scattering Spectra (Frequency in cm^{-1})

Cyclopropane [8]	Methylcyclopropyl ketone	Ethylcyclopropyl ketone [8]	Methylcyclopropyl carbinol	Cyclopropylcarbinol [9]
	248 (3)			
382 (very weak)	392 (2)	389 (medium)	372 (1)	364 (weak)
	468 (1)	473 (very weak)	489 (2)	483 (medium)
	523 (1)	570 (very weak)	509 (2)	
	688 (4)		711 (3)	
740 (weak)	737 (6)	762 (medium)	736 (4)	749 (very weak)
		792 (weak)	770 (2)	773 (medium)
				802 (medium)
866 (very weak)	816 (5)	824 (medium)	822 (4)	835 (medium)
	855 (1)			
	894 (5)	881 (strong)	885 (10)	900 (medium)
			919 (4)	927 (medium)
	952 (2)	964 (very weak)	953 (1)	962 (very weak)
				997 (medium)
1000 (weak)				
1022 (weak)	1024 (3)	1020 (medium)	1020 (1)	
1070 (weak)	1082 (1)	1092 (weak)	1078 (1)	
1120 (weak)	1111 (1)	1123 (weak)	1107 (1)	1101 (very weak)
1189 (very weak)	1187 (10)	1197 (very strong)	1197 (10)	1197 (very strong)
	1244 (2)	1250 (very weak)	1244 (2)	1256 (very weak)
	1327 (2)	1333 (weak)	1300 (2)	1336 (very weak)
	1379 (2)	1388 (weak)	1394 (1)	
1435 (medium)	1430 (4)	1418 (medium)	1435 (3)	1431 (medium)
1454 (medium)			1463 (3)	1465 (medium)
1504 (weak)		1554 (medium)		
	1695 (6)	1701 (medium)		
1873 (very weak)				
2854 (weak)			2877 (3)	2872±8 (medium)
	2913 (6)	2900±10 (medium)	2933 (3)	2921± 8 (medium)
2952 (weak)		2943 (medium)		2953±8 (medium)
		2979 (medium)	2977 (3)	
3011 (strong)	3009 (6)	3013 (strong)	3013 (8)	3011 (very strong)
3029 (strong)				
3080 (strong)	3092 (4)	3093 (medium)	3077 (4)	3076 (strong)
			3420 (8 wide)	

The frequency of 3420 cm^{-1} occurring in the spectrum of methylcyclopropyl carbinol belongs to the hydroxyl group.

Examination of the frequencies permits us to draw the conclusion that our method of preparation of methylcyclopropyl carbinol by reduction of methylcyclopropyl ketone with aluminium isopropylate leads to the formation of a single product. The three-membered ring remains intact during the process.

EXPERIMENTAL

Acetopropyl bromide. Acetopropyl alcohol with b.p. 105-107° at 20 mm was brominated by Lipp's method [10] by mixing it with 4 volumes of 50-55% hydrobromic acid. After standing for 8 hours at room temperature the solution was poured into the 4- or 5-fold volume of water. The bromide was extracted from the mixture with ether 3 times. The ether extract was dried over calcium chloride, the ether was driven off and the bromide distilled in vacuum. The bromide came over completely at 83-85° and 16 mm or at 105-107° and 60 mm. The distillation flask contained a very small amount of resin. Yield of bromide 55-58% of theory.

Methylcyclopropyl ketone was prepared by a slight modification of the method of Vagner [11]. The bromide prepared from acetopropyl alcohol was mixed with rather more than the calculated amount of powdered alkali and a little water. Amounts used for 25 g bromide were 12 g KOH and 3-4 ml water. The mixture was continuously and very thoroughly mixed by shaking the flask. Considerable heat was developed. The reaction was completed in 10 minutes. After addition of a further 3-5 ml water a crystalline precipitate of potassium bromide came down and the newly formed ketone separated in a layer. 100 ml water was added to the reaction mixture. The ketone was distilled off in steam. Further processing was precisely on the lines detailed by Vagner. Yield of crude ketone was 92-95% of theory. The conditions that we worked out for the performance of this reaction approximate to those of Rozanov [12], although in his experiments the yields of ketone were only 55-59%.

On distillation the main bulk of the ketone came over at 111-112.5°. The fraction coming over at 112-112.5° had the following constants: d_4^{20} 0.8987; n_D^{20} 1.4246; MR_D 23.90; calcd. 23.10. The exaltation value of 0.8 slightly exceeds the value of the increment for the three-membered ring. We consider this increase to be due to the above-noted pseudoconjugation.

The semicarbazone of the ketone had m.p. 121-122°. According to the literature it melts at 121.4-122.5° [13].

Methylcyclopropyl carbinol. 14 g methylcyclopropyl ketone was dissolved in 250 ml dry isopropyl alcohol and added to the aluminum isopropylate prepared from 14 g aluminum and 150 ml isopropyl alcohol with addition of 0.5 g mercuric chloride and 4 ml carbon tetrachloride [14]. The mixture was slowly heated on an oil bath to 110-115°. The acetone formed in the reaction was slowly distilled off with a dephlegmator. Distillation was continued until the last portions of distillate ceased to give a positive reaction for acetone with 2,4-dinitrophenylhydrazine. A solution consisting of 35 ml water and 100-150 ml isopropyl alcohol was added to the residue in the flask in small portions with good agitation. During this operation the flask was cooled with iced water. The reaction mixture was allowed to stand for a few hours, following which the precipitated aluminum hydroxide was filtered on a Buechner funnel. The residue on the filter was treated with dilute sulfuric acid (40 ml sulfuric acid to 250 ml water). The acid solution was extracted with ether. The ether extract was dried over potassium carbonate.

The filtrate, which contained the isopropyl alcohol and nearly the whole of the methylcyclopropyl carbinol, was fractionated. The following fractions were collected: 1) up to 82°; 2) 82-86°; 3) 86-119°; 4) 119-123° (methylcyclopropyl carbinol).

After the ether had been driven off, the ether extract was fractionated in the same temperature ranges. The corresponding fractions were combined. The yield of crude product amounted to 13.3 g or 92.6% of theory. After careful fractionation of all the fractions, a fraction was isolated with b. p. 121-122° in an amount equivalent to 87% of theory. A total of 86 g pure carbinol was obtained from 98 g ketone. For the purpose of more accurate characterization a fraction boiling at 122.4-122.6° at 759 mm was collected.

d_4^{20} 0.8885; n_D^{20} 1.43140; MR_D 25.16; calcd. 24.61; exaltation 0.55. [1])

γ^{20} = 23.35 dynes/cm; P found 223.4; calcd. 225 (for an increment of 16.7 for the three-membered ring). 0.2275 g substance; 0.5805 g CO_2; 0.2416 g H_2O. Found %: C 69.63; H 11.88. $C_5H_{10}O$. Calculated %: C 69.71; H 11.71.

The combination scattering spectra of methylcyclopropyl carbinol and methylcyclopropyl ketone obtained in our laboratory are also presented in Table 2.

SUMMARY

1. A convenient laboratory method is developed for the preparation of methylcyclopropyl carbinol and methylcyclopropyl ketone with the aid of aluminum isopropylate. The prepared carbinol is a homogeneous substance. Its yield is 87% of theory and might even be increased.

2. The combination scattering spectra of methylcyclopropyl carbinol and methylcyclopropyl ketone have been obtained.

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1) The increment for the three-membered ring in the carbinol has a somewhat low value, but this is entirely in accord with Henry's data for alcohols of the cyclopropane series.

THE PROBLEM OF THE STRUCTURE OF GUSTAVSON'S HYDROCARBON

II. THE STEPWISE SYNTHESIS OF SPIROPENTANE

Ya. M. Slobodin and I. N. Shokhor

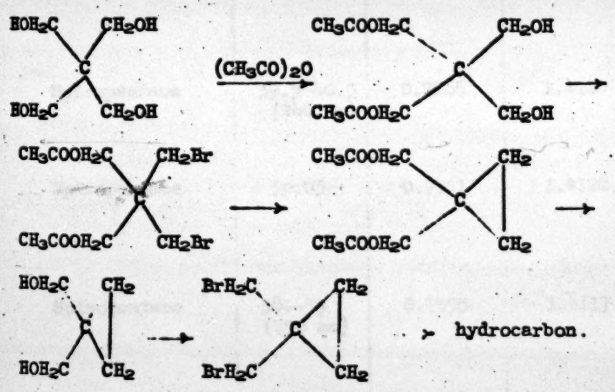
In the previous communication [1] we showed that reaction of zinc dust with tetrabromoneopentane under the conditions described by Gustavson [2] leads to formation of a hydrocarbon mixture not containing spiropentane and other hydrocarbons with a trimethylene ring. Examination of the combination scattering spectra revealed that the chief components of Gustavson's hydrocarbon are methylenecyclobutane and 2-methylbutene-1. A scheme was proposed for the transformation of tetrabromoneopentane into methylenecyclobutane which was similar to the bromohydrin rearrangement scheme described by Favorsky [3].

In 1944 Murray and Stevenson reacted zinc dust with tetrabromoneopentane in fused acetamide in presence of NaI and Na_2CO_3, and obtained a hydrocarbon mixture containing up to 40% spiropentane.

In 1946 Slabey [5] reacted zinc dust with tetrabromoneopentane in aqueous alcohol in presence of the same additives, and obtained a hydrocarbon mixture (up to 89% yield) containing up to 28% spiropentane. On replacing the alcohol by acetamide the yield of hydrocarbon fell to 36-38% and its spiropentane content was 47-60%.

In the present investigation a stepwise synthesis of spiropentane was performed by the method of Zelinsky and Kravets [6] with the objective of making a detailed study of the hydrocarbon which was assumed by the authors to be spiropentane.

Synthesis was effected according to the scheme:



The combination scattering spectra were used for characterization of the hydrocarbon and of the intermediate products of its synthesis.

The hydrocarbon prepared by us was not deliberately subjected to fractional distillation, but was merely distilled over metallic sodium. In this way the removal of any of the components of the reaction product was excluded.

Table 1 compares the properties of our hydrocarbon with those of hydrocarbons obtained by other authors.

The combination scattering spectrum of our hydrocarbon and the intensity of the spectral lines are in complete accord with the frequencies of methylenecyclobutane. We did not observe any frequencies that might have been asociated with

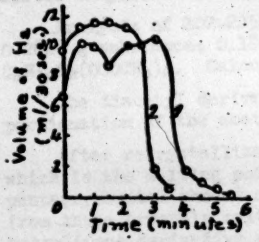
spiropentane.

TABLE 1

Hydrocarbon	Boiling point	d_4^{20}	n_D^{20}	Author and method of preparation
Gustavson's hydrocarbon	40°	0.7273 (18°)	1.41255 (18.5°)	Gustavson [2] dehalogenation of tetrabromoneopentane in aqueous alcohol
Methylenecyclobutane	42 (749 mm)	0.7360 (23°)	1.41738 (23°)	Filipov [7] higher fraction of Gustavson's hydrocarbon
Hydrocarbon prepared in the present investigation	41.5–42.5 (768 mm)	0.7357	1.41620	Stepwise debromination of tetrabromoneopentane
Methylenecyclobutane	41.6–41.9 (752 mm)	0.7326	1.4158	Murray and Stevenson [4] by fractionation of the hydrocarbon prepared in fused acetamide
Methylenecyclobutane	42.22	0.7401	1.42087	Slabey [5] by fractionation of the hydrocarbon prepared in alcohol in presence of NaI and Na_2CO_3
Spiropentane	39.5–40.5 (746 mm)	0.7266	1.4120	Zelinsky and Kravets [6] stepwise dehalogenation of tetrabromoneopentane
Spiropentane	39.03	0.7551	1.4122	Slabey [5] by fractionation of the hydrocarbon prepared in presence of NaI and Na_2CO_3
Spiropentane	38–39 (750 mm)	0.7555	1.4117	Murray and Stevenson [4] by fractionation of the hydrocarbon prepared in fused acetamide

In table 2 are detailed the combination scattering spectra of our hydrocarbon, of methylenecyclobutane and of spiropentane.

Our hydrocarbon and also Gustavson's hydrocarbon were subjected to hydrogenation by Lebedev's method [8]. A break appears on the hydrogenation curve of Gustavson's hydrocarbon. The point of inflection corresponds to the start of hydrogenation of a second component of the mixture. By contrast, our hydrocarbon was hydrogenated to the end at constant velocity. Its hydrogenation curve is reminiscent of the hydrogenation curves of pure hydrocarbons (see diagram).



Hydrogenation curves of hydrocarbons.

1—Gustavson's hydrocarbon; 2—hydrocarbon prepared in this study.

TABLE 2

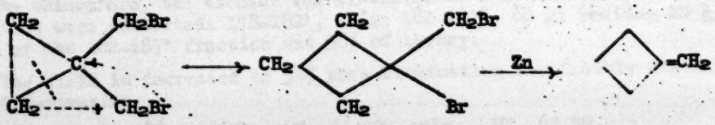
Combination Scattering Spectra

(Frequencies in cm^{-1})

Methylenecyclobutane [4]	Hydrocarbon obtained in present study	Spiropentane [4]
354 (23)	353 (4)	305 (4)
373 (13)	371 (2)	
		581 (16)
		613 (4)
657 (20)	657 (5)	
		779 (4)
873 (14)	873 (2)	872 (30)
907 (20)	908 (3)	
957 (72)	955 (8)	
	986 (2)	
		1033 (50)
		1150 (1)
1191 (11)	1191 (2)	
1391 (20)	1391 (2)	1397 (5)
1428 (20)	1424 (2)	1426 (10)
1679 (48)	1679 (8)	
2826 (4)	2828 (1)	2836 (0.4)
2861 (11)	2856 (1)	
		2891 (c1)
2902 (60)	2906 (8)	
2921 (71)	2924 (4)	
2952 (81)	2958 (8)	
2986 (100)	2991 (8)	2991 (100)
3072 (18)	3068 (2)	3065 (30)

Ozonolysis of our hydrocarbon gave cyclobutanone and formic acid. No other products were detected.

Consequently our results show that the stepwise synthesis yields methylenecyclobutane without appreciable amounts of other hydrocarbons. The formation of methylenecyclobutane in our synthesis confirms the scheme of Favorsky and Batalin [9] for synthesis of this hydrocarbon:



The process of isomerization with formation of the cyclobutane ring is effected in this last phase of the synthesis. In addition we must assume the possibility of isomerization also at earlier phases of the synthesis.

The combination scattering spectra of dimethylolcyclopropane and its dibromide are characterized by great complexity and contain the characteristic frequencies of both a three-membered and a four-membered ring with a great similarity in the frequencies for the carbon skeleton.

Thus partial isomerization already takes place during the preparation of the ester of dimethylol cyclopropane.

EXPERIMENTAL

Propanediol-1,3-dimethylol-2,2-diacetate. In a flask fitted with a reflux condenser was placed a mixture of 136 g pentaerythritol and 102 g acetic anhydride. The flask was heated to gentle boiling for a period of 8 hours. After removing the unreacted pentaerythritol (28 g) and distilling off the acetic acid and the residual acetic anhydride, the reaction products were distilled in vacuum at 12 mm. Fractions collected were: 165-196°, 20 g; 196-205°, 120 g; 205-212°, 13 g; residue, 15 g.

The 196-205° fraction was distilled a second time at 12 mm to give 3 g boiling at 198-202°; 110 g at 202-205°; and 6 g boiling above 205°.

The yield of the 202-205° fraction was 50% of theory calculated on the basis of the diacetyl derivative. The yield depends on the quality of the acetic anhydride and may be easily raised to 64%.

Analysis of 202-205° (12 mm) fraction for acetyl content [10]. 0.3257, 0.2826 g substance: 0.1800, 0.156 g CH_3COOH. Found%: CH_3COOH 55.3, 55.2. $C_5H_{10}O_2(OCOCH_3)_2$. Calculated%: CH_3COOH 54.5. M (Rast) 222; calc. 220.

The diacetyl derivative partly crystallized when kept owing to disproportionation of the acetyl groups.

After recrystallization from alcohol the crystals melted at 251-253°, which is the melting point of pentaerythritol. A mixed sample with pentaerythritol showed no depression. The dibenzylidene derivative prepared from these crystals melted at 157-159°. A mixed melting specimen with the dibenzylidene derivative prepared from pure pentaerythritol also melted without depression.

The fraction boiling at 165-196° rapidly crystallized. The m. p. of the crystals was 75-76°. Analysis showed an acetic acid content of 74.9%. This corresponds to a mixture of approximately equal parts of the tri- and tetraacetates of pentaerythritol. Treatment of this product with acetic anhydride leads to the pure tetraacetate of pentaerythritol with m. p. 84°.

1,3-Dibromopropane-2,2-dimethylol diacetate. Into a round-bottomed flask cooled with ice were introduced 110 g diacetyl derivative of pentaerythritol, 31 g red phosphorus and 100 ml chloroform. The calculated amount of bromine was slowly run in from a dropping funnel. At the conclusion of the reaction the mixture was poured into iced water. The lower layer was isolated, washed with soda solution and water, and dried over fused sodium sulfate. After distilling off the chloroform, the bromide was distilled in a 12 mm vacuum. The following fractions were collected: 178-182°, 12 g; 182-187°, 66 g; residue 20 g. The yield of the 182-187° fraction was 38% of theory.

The yield is increased to 54% when brominating the freshly distilled diacetyl derivative.

d_4^{20} 1.6518; n_D^{20} 1.50591. MR_D 62.09; calc. MR_D 62.59.

0.2186 g substance: 0.2549 g AgBr. Found%: Br 46.15; M 351 (cryoscopically). $C_9H_{14}O_4Br_2$. Calculated%: Br 46.24; M 346.

1,1-Dimethylolcyclopropane diacetate. Into a flask fitted with a stirrer and a reflux condenser were introduced 190 g dibromide, 150 ml 96° alcohol, 15 ml water and 50 g zinc dust. Reaction set in spontaneously and proceeded with considerable evolution of heat. The mixture was subsequently heated on the boiling water bath for 2 hours. The precipitate was filtered off. The

alcoholic solution was diluted in a separating funnel with a large volume of water until oily drops appeared. The oil was extracted with ether. The ether layer was isolated and dried over sodium sulfate. After distilling off the ether, the oil was distilled in vacuum at 30 mm. Fractions: 135-137°, 45 g; 137-142°, 5 g. The yield of the first fraction was 44.1% of the theoretical.

d_4^{20} 1.0817; n_D^{20} 1.44456; γ^{20} 47.3. Found: MR_D 45.72; P 411.3; M 181. $C_9H_{14}O_4$ (with a three-membered ring). Calculated: MR_D 45.57; P 419.3. M 186. 0.2039 g substance: 0.4328 g CO_2; 0.1430 g H_2O. Found%: C 57.92; H 7.81. $C_9H_{14}O_4$. Calculated %: C 58.02; H 7.59.

1,1-Dimethylolcyclopropane. The diacetyl ester of dimethylolcyclopropane was saponified by digesting 20 g with saturated potassium carbonate solution for 6 hours. After cooling, the glycol formed was salted out with potassium carbonate and repeatedly extracted with ether and then with chloroform. After drying over fused potassium carbonate and distilling off the solvent, the glycol was distilled in a 12 mm vacuum. Fractions: 118-123°, 0.5 g; and 123-127°, 6 g. The yield of the second fraction was 55% of theory. The glycol partially crystallized.

d_4^{20} 1.0710; n_D^{20} 1.46435; γ^{20} 38.64 dynes/cm. MR_D 26.31; P 237.6; calc. MR_D 26.80; P 238.9; 0.1686 g substance: 0.3631 g CO_2; 0.1501 g H_2O; 0.0980 g substance: 45 ml CH_4 (0°, 760 mm). Found%: C 58.77; H 9.96; OH 34.9 $C_5H_8(OH)_2$. Calculated%: C 58.82; H 9.88; OH 33.3.

The low yield of glycol (55%) by saponification with potassium carbonate is bound up in large measure with losses during extraction. We therefore later modified the method of extraction of the glycol. The ester of dimethylolcyclopropane formed by the action of zinc dust on the corresponding bromide was separated from the excess of zinc dust; without further separation the mixture was then saturated with gaseous ammonia at 0°. Saturation was followed by the formation in the flask of a coarsely crystalline precipitate of the complex compound which was easily separated. The solution was again saturated with ammonia and left at room temperature for 2-3 days. After completion of the reaction the alcohol was distilled off from the mixture and the glycol formed was distilled in vacuum. The glycol obtained in this manner had b. p. 125-127° at 12 mm. It was contaminated with acetamide which was difficult to eliminate, but it was quite suitable for further working up. The yield of crude glycol by this method, based on the original ester, was nearly quantitative.

1,3-Dibromodimethylcyclopropane. The glycol was treated with PBr_3 in presence of pyridine [12]. 26 g glycol was mixed with 5 g pyridine and slowly run from a dropping funnel into a flask containing the calculated amount of PBr_3. At the conclusion of the reaction the mixture was poured into cold water. The bromide was extracted with ether. The ether solution was washed with soda and then with water, and dried over calcium chloride. After the ether had been distilled off, the bromide was distilled in vacuum at 22 mm. Fractions: up to 83°, 2 g; 83-87°, 20 g. The yield of the second fraction was 43% of theory. Its constants were as follows:

d_4^{20} 1.7895; n_D^{20} 1.53643 γ^{20} 37.94 dynes/cm. MR_D 39.75; P 316. Calc. MR_D 39.32; P 313.5. 0.5201 g substance: 0.8516 g AgBr (Carius). Found%: Br 69.69. $C_5H_8Br_2$ (with three-membered ring). Calculated %: Br 70.16.

Preparation of the hydrocarbon. Into a Wurtz flask fitted with a dropping funnel and a condenser were introduced 10 g zinc dust and 50 ml 94° alcohol. A solution of 25 g bromide in alcohol was slowly run in from the dropping funnel. The reaction usually commenced spontaneously. The flask was subsequently heated

on the water bath. The hydrocarbon formed was accordingly removed at once from the sphere of reaction. The loss of alcohol was made good throughout the whole period of reaction. The distillate was poured into iced water. The hydrocarbon was separated, dried over calcium chloride and distilled several times. The final distillation was performed over metallic sodium. The boiling point of the hydrocarbon was 41.5-42.5° (768 mm). Yield 3.5 g or 47% of theory. In all four portions of bromide were worked up.

d_4^{20} 0.7357; n_D^{20} 1.4162; γ^{20} 20.37 dynes/cm. Found: MR_D 23.21; P 196.4. C_5H_8 (with a four membered ringand a double bond). Calculated: MR_D 23.22;[1] P 195.6.

Hydrogenation of the hydrocarbon was performed by the Lebedev method with platinum oxide as catalyst. After reduction the hydrocarbon was collected in a duck. The weight of hydrocarbon was 0.2600 g. It absorbed 74 ml hydrogen or 90% of theory. Measurements of the hydrogen consumption were made every half minute (9.6; 11; 11.2; 11.4; 11.2; 10.2; 1.8; 0.2).

Gustavson's hydrocarbon was hydrogenated under the same conditions for the purpose of comparison. Weight of hydrocarbon 0.300 g. Hydrogen absorbed was 92 ml or 93% of theory. Measurements of hydrogen consumption every half minute: 6.6; 10; 10; 9.6; 8.4; 10; 10; 10.4; 8.8; 2.0; 1.4; 0.6; 0.2.

Ozonization of the hydrocarbon was effected in chloroform solution at -70°, using 1 g hydrocarbon and 3% ozone. The ozonide was extremely unstable and readily decomposed even on exposure to moist air. Its decomposition and working up were performed in the usual manner.

The neutral portions extracted from alkaline solution gave with 2,4-dinitrophenylhydrazine a crystalline precipitate which melted at 138-140°. After crystallization from alcohol the m.p. was 145°, which corresponded to the dinitrophenylhydrazone of cyclobutanone (the literature [14] gives 146.3-146.7°).

Formic acid was detected after acidification of the alkaline solution and was determined by the calomel method.

The combination scattering spectrum of the hydrocarbon is detailed above.

SUMMARY

1. Stepwise synthesis of spiropentane leads to the formation of methylenecyclobutane which was identified by its physical and chemical properties and by spectroscopic data.

2. Spiropentane is not formed due to isomerization of the three-membered ring into a four-membered one at various stages of the synthesis.

3. The scheme for isomerization of 1,3-dibromodimethylcyclopropane proposed by Favorsky was confirmed.

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THE ACTION OF HALO-SUBSTITUTED ETHERS ON THE SODIUM SALTS OF DI-β-ALKOXY ETHYL PHOSPHOROUS ACIDS

V. S. Abramov and E. A. Militskova

One of the most interesting aspects of the chemistry of organophosphorus compounds is that of the double decomposition reactions of salts of dialkyl phosphorous acids with various halo derivatives. The double decomposition usually gives esters of alkyl phosphinic acids according to the equation

$$(RO)_2PONa + R'Hal = (RO)_2P(R')=O + NaHal.$$

This equation is general for the majority of reactions and may thus be regarded as a rule, although there are exceptions to it.

Triaryl chloromethanes react normally with sodium diethyl phosphite to give an ester of triaryl methylphosphinic acid, whereas triaryl bromomethanes and sodium diethyl phosphite give free radicals [1]. The silver salt of diethyl phosphorous acid reacts normally with triphenyl bromomethane to form an ester of triphenylmethyl phosphinic acid, whereas triphenylchloromethane gives mixed esters of phosphorous acids [2]. Phenyl xanthyl chloride and bromide and phenyl and tolyl cyclopentadienyl bromides react with sodium diethyl phosphite to give free radicals. Consequently, in the course of the double decomposition of halo derivatives with salts of dialkyl phosphorous acids, a variegated picture is observed depending upon the nature of the metal in the salt, the nature of the halide, the structure of the radical and the experimental conditions [2].

Not only halo hydrocarbons but also halo derivatives with mixed functions can be brought into reaction with salts of dialkyl phosphorous acids. A. E. Arbuzov and A. N. Dunin [3] synthesized phosphocarboxylic acids by the action of halo-substituted acids on esters of phosphorous acid. Nylen [4] performed the reaction with sodium diethyl phosphite and found that the reaction proceeds anomalously. In a study of the action of chloro- and bromomethyl ethers on the sodium salts of various dialkyl phosphorous acids, we have observed an interesting phenomenon — the formation of a salt of an ester of an alkyl phosphinic acid if the reaction products are distilled from the reaction flask without separation of the sodium chloride or bromide. Sodium bromide is the more reactive and gives ester salts in all the cases of action of bromo-substituted ethers on sodium dialkyl phosphite which have been investigated, whereas sodium chloride did not form ester salts in certain cases. Abramov and Azanovskaya [5] studied the action of dichloro- and dibromomethyl ethers on sodium diethyl phosphite and found that in this case ester salts were formed both with the sodium chloride and the sodium bromide formed in the reaction. Abramov and Sergeeva [6] examined the action of chloro- and bromomethyl benzyl ethers on sodium diethyl and dibutyl phosphite. Ester salts of benzyloxymethyl phosphinic acid are formed in this case both with sodium chloride and sodium bromide. It was also demonstrated in the investigation that an ester salt is formed with equal success when using the ethyl ester of benzyloxymethyl phosphinic acid and the sodium chloride or the sodium bromide separated from the reaction.

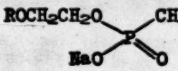
In the present paper we submit the results of a study of the action of various halo-substituted ethers on the sodium salts of di- β -methoxy- and di-β-ethoxyethyl esters of phosphorous acids. For this purpose we prepared di-β-methoxy and di-β-ethoxyethyl phosphorous acids by the action of phosphorus trichloride on the monoxomethyl and monoethyl ethers respectively of

ethylene glycol. The prepared di- β -alkoxyethyl phosphorous acids are colorless, readily mobile, odorless liquids with the following physical constants (table 1).

TABLE 1

Formula	Boiling point	n_D^{20}	d_4^{20}	MR_D Found	MR_D Calculated
$(CH_3OCH_2CH_2O)_2P(=O)H$	150—151° at 13 mm	1.4310	1.158	44.0	43.92
$(C_2H_5OCH_2CH_2O)_2P(=O)H$	156—157° at 13 mm	1.4302	1.088	53.68	53.28

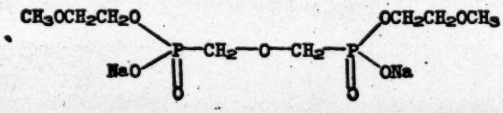
Di- β -methoxy- and di- β -ethoxyethyl phosphorous acids react in ethereal solution with metallic sodium. The resultant sodium di- β -methoxy- and di- β -ethoxyethyl phosphites react with various halo-substituted ethers — monobromomethyl, bromomethyl ethyl, bromomethyl propyl and chloromethyl butyl. The reaction generally proceeds with separation of sodium bromide or chloride. When the reaction products are distilled from the reaction flask without separating the sodium halide, in all the investigated cases ester salts of alkoxymethyl phosphorous acids of the composition



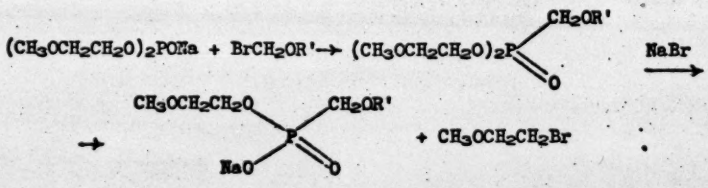
are formed.

R = methyl or ethyl; R' = methyl, ethyl, propyl and butyl.

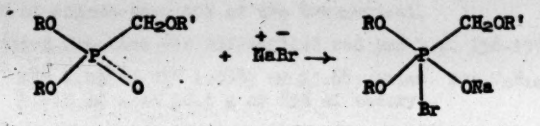
Symmetrical dibromo-substituted dimethyl ether reacts with sodium di- β -methoxyethyl phosphite. Distillation of the reaction products from the reaction mass without prior separation of the sodium bromide gives an ester salt of diphosphonomethyl ether with the composition



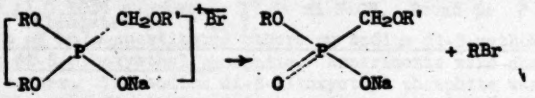
Halo-substituted ethers evidently react with sodium dialkyl phosphites according to the equation:



A mechanism for the formation of ester salts during the action of sodium bromide or chloride on esters of alkyl phosphinic acids had not previously been advanced. We suggest the following approximate course of these reactions: The reaction undoubtedly proceeds at the P=O bond which, on the basis of a determination of the interatomic distances for some phosphorous compounds [7], may be assumed to have a large amount of double bond character. The sodium halide molecule combines at the P=O bond and forms an addition product according to the scheme



or



The halogen may be combined with phosphorus either by a covalent or an ionic bond of the phosphonium type.

The alkyl halide distills over during the reaction, and therefore the reaction is directed towards the formation of a salt as the final product.

EXPERIMENTAL

Preparation of di-β-methoxyethyl phosphorous acid. Into a round-bottomed flask provided with a stirrer and a reflux condenser was introduced 230 g "methyl cellosolve", and to this with stirring and cooling was run in gradually 138 g phosphorous trichloride from a dropping funnel. After the whole of the phosphorous trichloride had been added, the stirrer was allowed to run for an additional half hour. The hydrogen chloride was then driven out of the reaction flask with a current of dry air until the volume of the contents was constant. The residue was fractionated in vacuum.

Fractionation: First fraction 35-40° at 20-17 mm, 20.2 g; second fraction 140-154° at 17 mm, 14.6 g; third fraction 154-157° at 17 mm, 135.3 g. The first fraction was methyl-β-chloroethyl ether with the constants: n_D^{20} 1.4110; d_4^{20} 1.039; MR_D 22.99; calcd. 22.71. The yield of chloroether (21.5% of the theoretical) was low, apparently due to large losses during fractionation and removal of hydrogen chloride. The second and third fractions were redistilled and gave a product with b.p. 150-151° at 13 mm and the constants:

n_D^{20} 1.4310; d_4^{20} 1.158; MR 44.0; calcd. for $C_6H_{15}O_5P$ 43.92

The yield of di-β-methoxyethyl phosphorous acid was 140 g or 70% of theory.

0.0911 g substance: 30.3 ml NaOH (T = 0.01754, 1 ml corresponds to 0.000485 g phosphorous). 0.1192 g substance: 39.5 ml NaOH. Found %: P 16.1, 16.0 (Neumann's method). $C_6H_{15}O_5P$. Calcd. %: P 15.65.

Preparation of di-β-ethoxyethyl phosphorous acid. The "ethyl cellosolve" required for the preparation was prepared by the action of ethylene chlorhydrin with b.p. 112-130° on sodium alcoholate. To 108.5 g "ethyl cellosolve" (b.p.

134-136° and n_D^{20} 1.4023) was added, with stirring and cooling, 55.3 g phosphorous trichloride. Fractionation was performed after the hydrogen chloride had been removed with a stream of dry air. Fractions: 1) 35-40° at 17-16 mm, 14.6 g; 2) 40-159° at 16-15 mm, 8.5 g; 3) 159-160° at 14 mm, 78 g. The first fraction (β-chloroethyl ether) had the constants:

n_D^{20} 1.4110; d_4^{20} 0.991; MR 26.27; calcd. 26.62.

Yield of chloroether 40% of the theoretical.

The third fraction was redistilled and had b.p. 156-157° at 13 mm and the constants:

n_D^{20} 1.4302; d_4^{20} 1.088; MR 53.68; calcd. for $C_8H_{19}O_5P$ 53.28.
Yield of acid 58.5 g or 65% of theory.

0.1182 g substance: 19.92 ml NaOH. (T = 0.02843; 1 ml phosphorus (0.000746 g) 0.1086 g subst.; 17.94 ml NaOH. Found %: P 13.24, 13.6. $C_8H_{19}O_5P$. Calculated %: P 13.7.

Action of halo-substituted ethers on sodium di-β-methoxyethyl phosphite and sodium di-β-ethoxyethyl phosphite. Experiments were conducted in the following manner. The sodium di-β-alkoxyethyl phosphite was first prepared. 30 ml of ether was first placed in a small flask and 0.6 g metallic sodium was forced in in the form of wire. Through a dropping funnel was then poured 5 g di-β-methoxyethyl phosphorous acid or 6 g di-β-ethoxyethyl phosphorous acid. The flask was heated on the water bath until the sodium wire had completely reacted. To the resultant sodium di-β-methoxyethyl or di-β-ethoxyethyl phosphite was added the equivalent amount of halo-substituted ether. This was quickly followed by the separation of white, slowly settling sodium chloride or bromide. The flask was again heated on the water bath for a period of half an hour under a reflux condenser. The ether was then distilled off and the residual products were fractionated in vacuum. There usually remained in the flask a white residue of the ester salt of alkoxymethyl phosphinic acid which was purified by dissolution in absolute alcohol and precipitation with dry ether. The distilled portion always consisted of methyl-β-chloroethyl ether when the starting material was di-β-methoxyethyl phosphorous acid, or of β-chloroethyl ether when the starting material was di-β-ethoxyethyl phosphorous acid; also present were minor amounts of the corresponding ester of alkoxymethyl phosphinic acid in some experiments. Results of experiments with sodium di-β-methoxyethyl phosphite are given in Table 2 and those with sodium di-β-ethoxyethyl phosphite in Table 3.

Action of dibromomethyl ether on sodium di-β-methoxyethyl phosphite. To the sodium di-β-methoxethyl phosphite prepared from 0.8 g metallic sodium in 40 ml dry ether and 7 g di-β-methoxyethyl phosphorous acid was run in 3.8 g dibromomethyl ether. The reaction products were fractionated in vacuum. An insignificant amount came over. The residue in the flask was a white, viscous mass which was purified by dissolution in absolute alcohol. Weight of crude salt 5.35 g or 83.5% of theory.

0.1092 g substance: 23.2 ml NaOH (T = 0.02843). Found %: P 16.64. $C_8H_{18}O_9P_2Na_2$. Calculated %: P 16.94.

TABLE 2

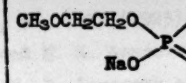
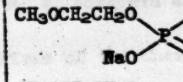
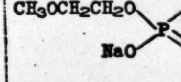
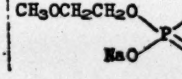
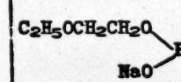
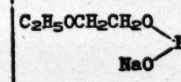
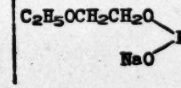
No.	Halo-substituted ether	Ester salt of phosphinic acid obtained	Yield of salt (%)	Analysis for Phosphorous	
				calculated	found
1	$ClCH_2OCH_3$	No salt obtained			
2	$BrCH_2OCH_3$		Not calculated	15.09	14.88
3	$BrCH_2OC_2H_5$		66	14.1	14.3
4	$BrCH_2OC_3H_7$		70	13.24	13.27; 13.42
5	$ClCH_2OC_4H_9$		65	12.5	12.3; 12.5

TABLE 3

No.	Halo-substituted ether	Ester salt of phosphinic acid obtained	Yield of salt (%)	Analysis for Phosphorous	
				calculated	found
1	$BrCH_2OCH_3$		38	14.09	13.61
2	$BrCH_2OC_2H_5$		72	13.24	13.48; 13.7
3	$BrCH_2OC_3H_7$		89	12.5	12.46; 12.03

SUMMARY

1. Di-β-methoxyethyl phosphorous and di-β-ethoxyethyl phosphorous acids have been prepared.

2. The obtained acids form sodium salts with metallic sodium. A study was made of the action on the sodium salts of di-β-methoxyethyl phosphorus and di-β-ethoxyethyl phosphorous acids of the ethers: monobromomethyl ether; monobromomethyl ethyl ether; monobromomethyl propyl ether; monochloromethyl butyl ether; and dibromomethyl ether. There were obtained the ester salts of the

corresponding phosphinic acids.

3. A mechanism for the reactions which take place is proposed.

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N-ARYLAMIDES OF HYDROXY CARBOXYLIC ACIDS AND THEIR TRANSFORMATION INTO HETEROCYCLIC COMPOUNDS

VIII. INTRAMOLECULAR CONDENSATION OF ARYLAMIDES OF m,m-DITOLYL GLYCOLIC ACID

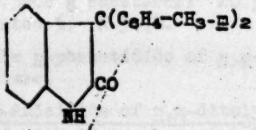
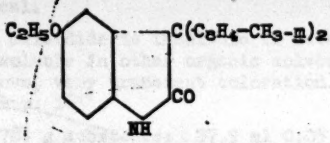
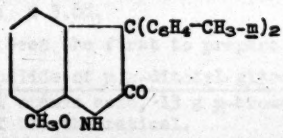
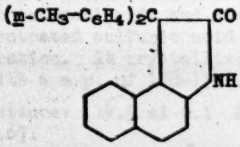
P. A. Petyunin and I. S. Berdinsky

We have studied the condensation of ArNHCOC(OH)($C_6H_4CH_3$-m)$_2$ where Ar = C_6H_5-, p-$C_2H_5OC_6H_4$-, o-$CH_3OC_6H_4$- and β-$C_{10}H_7$-.

The properties of the prepared compounds are tabulated below.

Not a single one of the listed compounds has been described in the literature. This is because the known literature methods for preparation of 3,3-diaryl derivatives of oxindole only permit the formation of compounds with para-substituted aryl groups.

m-Tolylisatin and Its Derivatives

No.	Formula	Melting Point
1		188.5°
2		220°
3		213°
4		179°

EXPERIMENTAL

Anilide of m,m-ditolyl glycolic acid. Reactants were 3.86 g (1 mole) oxanilic ether, 17 g (5 moles) m-bromotoluene and 2.4 g magnesium. Yield 4.7 g or 66.5% of the theoretical yield.

The anilide is insoluble in water; it dissolves in the majority of common organic solvents. It gives a transient brown color with concentrated sulfuric acid. It crystallizes from dilute alcohol in colorless needles which form clusters. M.p. 138.5°-139.5°.

0.2435 g substance: 7.74 ml 0.1 N H_2SO_4. Found %: N 4.45. $C_{22}H_{21}O_2N$. Calculated %: N 4.23.

The anilide of m,m-ditolyl glycolic acid has not been described previously.

p-Phenetidide of m,m-ditolyl glycolic acid. Starting materials: 4 g ethyl ester of p-ethoxyoxanilic acid, 13 g m-bromotoluene and 1.8 g magnesium. Yield 5.1 g or 80.6% of the theoretical.

The phenetidide is insoluble in water, soluble with difficulty in gasoline, and readily soluble in other common solvents. It gives a brown color with concentrated sulfuric acid which rapidly disappears. It crystallizes from aqueous alcohol in colorless platelets. At 126-127° the substance becomes very moist, then solidifies and finally melts at 142°. After drying to constant weight it melts at 142°.

Determination of water of crystallization (100-110°).

0.4586 g substance: 0.0052 g H_2O. Found %: H_2O 1.13. $C_{24}H_{25}O_3N$. Calculated %: H_2O 1.18.

A portion of the dehydrated substance was analyzed for nitrogen.

0.3802 g substance: 20.5 ml 0.05 N H_2SO_4. Found %: N 3.78. $C_{24}H_{25}O_3N$. Calculated %: N 3.78.

The p-phenetidide of m,m-ditolyl glycolic acid has not been described in the literature.

o-Anisidide of m,m-ditolyl glycolic acid. 3.8 g o-Methoxyoxanilic ester was reacted with 13 g m-bromotoluene and 1.8 g magnesium. Yield 4.8 g or 78% of the theoretical.

The anisidide is insoluble in water, soluble with difficulty in gasoline and readily soluble in other organic solvents. With concentrated sulfuric acid it gives a red-brown, very transient coloration. It crystallizes from alcohol in colorless prisms, m.p. 165°.

0.4784 g substance: 27.9 ml 0.05 N H_2SO_4. Found %: N 4.08. $C_{23}H_{23}O_3N$. Calculated %: N 3.88.

We have been the first to prepare the o-anisidide of m,m-ditolyl glycolic acid.

β-Naphthalide of m,m-ditolyl glycolic acid was prepared from 4.1 g ethyl ester of β-naphthyl oxamic acid, 13 g m-bromotoluene and 1.8 g of magnesium. Yield 4.9 g or 76.2% of the theoretical.

The substance is insoluble in water and ether; it dissolves with difficulty in alcohol and carbon tetrachloride and readily in benzene and glacial acetic acid. It dissolves in concentrated sulfuric acid with formation of a reddish-brown, rapidly disappearing coloration. It crystallizes from glacial acetic acid in colorless, slender needles with a m.p. of 178-179°.

0.5634 g substance: 14.9 ml 0.1 N H_2SO_4. Found %: N 3.7. $C_{28}H_{23}O_2N$. Calculated %: N 3.67.

The β-naphthalide of m,m-ditolyl glycolic acid has not been described in the literature.

3,3-Di-(m)-tolyl oxindole (m-tolylisatin). To a solution of 1.5 g of the anilide of m-toluic acid in 15 ml glacial acetic acid was added concentrated sulfuric acid until a brown coloration had ceased to be formed. Yield 1.41 g or nearly 100%

of the theoretical. The compound dissolves in the majority of the common organic solvents. Colorless needles from dilute acetic acid, m.p. 188.5°.

0.1565 g substance: 0.4837 g CO_2; 0.0832 g H_2O. 0.3402 g substance: 10.75 ml 0.1 N H_2SO_4. Found %: C 84.35; H 5.95; N 4.42. $C_{22}H_{19}ON$. Calculated %: C 84.34; H 6.07; N 4.47.

3,3-Di-(m)-tolyl-5-ethoxyoxindole. Starting materials were 2 g p-phenetidide of m,m-ditolyl glycolic acid, dissolved in 25 ml glacial acetic acid, and 25 ml concentrated sulfuric acid. Yield 1.8 g or about 90% of theoretical. The compound is soluble in alcohol, ether, benzene, carbon tetrachloride, etc. It crystallizes from alcohol in fine needles collected in the form of sheaves. M.p. 220°.

0.2098 g substance: 12.8 ml 0.05 N H_2SO_4. Found %: N 4.27. $C_{24}H_{23}O_2N$. Calculated %: N 3.97.

3,3-Di-(m)-tolyl-7-methoxyoxindole was prepared by adding concentrated sulfuric acid to a solution of 1.5 g anisidide of m,m-ditolyl glycolic acid in 20 ml acetic acid. Yield 1.33 g or 90.4% of theoretical. Crystallizes from acetic acid in colorless needles with m.p. 213°.

0.4406 g substance: 24.5 ml 0.5 N H_2SO_4. Found %: N 3.89. $C_{23}H_{21}O_2N$. Calculated %: N 4.08.

3,3-Di-(m)-tolyl-4,5-benzoxindole. (3,3-Di-(m)-tolyl-β-naphthoxindole). Condensation of 2 g of the β-naphthalide of m,m-ditolyl glycolic acid gave 1.8 g substance or 94.7% of theoretical. The substance is soluble in the majority of organic solvents. It crystallizes from alcohol in colorless needles which form clusters. At 148-150° it becomes very moist, then solidifies, and finally melts at 179°.

After drying to constant weight (at 100-110°) it melts, after passing through a softening phase, at 179°.

A portion of the dried compound was analyzed for nitrogen.

0.3574 g substance: 20.7 ml 0.05 N H_2SO_4. Found %: N 4.05. $C_{26}H_{21}ON$. Calculated %: N 3.85.

SUMMARY

1. A method was developed for the preparation of m-tolylisatin and its derivatives. A series of compounds not described in the literature was thereby prepared.

2. A series of arylamides of m,m-ditolyl glycolic acid were prepared and their properties investigated.

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Organic Chemical Laboratory of the
Molotov Pharmaceutical Institute

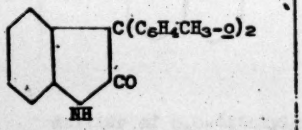
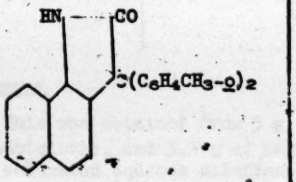
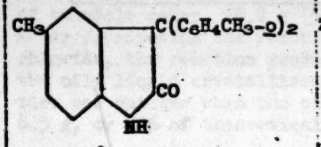
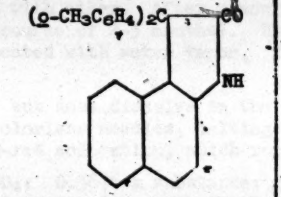
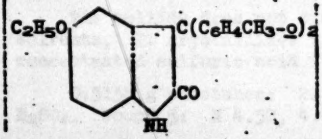
N-ARYL AMIDES OF HYDROXYCARBOXYLIC ACIDS AND THEIR CONVERSION TO HETEROCYCLIC COMPOUNDS

IX. INTRAMOLECULAR CONDENSATION OF ARYL AMIDES OF o,o-DITOLYLGLYCOLIC ACID.

P. A. Petyunin and I. S. Berdinsky

The aryl amides of o,o-ditolylglycolic acid are converted by sulfuric acid into the corresponding products of oxindole and naphthoxindole. These compounds may also be obtained successfully with red lead during the separation of the corresponding aryl amide. For this the impure product of interaction of a magnesium-organic compound with the ester of the N-aryloxamic acid was dissolved in glacial acetic acid, decolorized with activated carbon, and then used for condensation. The reaction is rapid, and the product is obtained in good yield. The properties of the products obtained are set forth in Table 1. None of these compounds has been described in the literature, which can be explained by the absence of any method for their preparation.

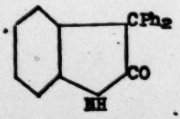
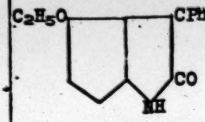
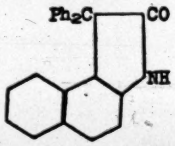
Table 1

No.	Formula	M.p.	No.	Formula	M.p.
1		306°	4		254°
2		296-297°	5		300°
3		285°			

The melting points of the ditolyl derivatives of oxindole depend on the position of the methyl group. They fall in the order o > p > m (Table 2).

On the whole, the intramolecular condensation of the aryl amides of α-hydroxy acids, in the presence of sulfuric acid, is quite smooth. In contrast to the usual method of obtaining 3,3-diaryl-substituted oxindoles, it opens up the possibility of preparing a product with the aryl group substituted in any position. The almost quantitative yield of the reaction products, their specificity, and the high reaction rate suggest that the intramolecular condensation of aryl amides of α-hydroxy acids is the most general method for the preparation of 3,3-diaryl-substituted oxindoles.

Table 2

No.	Formula	Position of CH_3 in the phenyl groups (Ph)		
		o	p	m
1		306°	200-201°	188.5°
2		285	263	220
3		300	246.5	179

EXPERIMENTAL

Anilide of o,o-ditolylglycolic acid. This was obtained from 5 g (1 mole) of oxindole ester, 28.2 g (5 moles) of o-iodotoluene, and 3.1 g of magnesium. After decomposing the reaction mass with a saturated aqueous solution of ammonium chloride, the reaction product was extracted with ether. After removing the solvent, the oily liquid crystallized slowly (in the course of 2-3 months). The crystallization was quicker when the oily liquid was treated with water vapor. The yield was 6.3 g, or 73% of theoretical.

The anilide does not dissolve in water, but does dissolve in the usual organic solvents. It crystallizes from alcohol as colorless needles, melting at 133°. In concentrated sulfuric acid it gives a cherry-red coloration, which rapidly disappears.

0.3136 g substance: 20.3 ml 0.05 N H_2SO_4; 0.3876 g substance: 24.8 ml 0.05 N H_2SO_4. Found %: N 4.52, 4.48. $C_{22}H_{21}O_2N$. Calculated %: N 4.23.

p-Toluidide of o,o-ditolylglycolic acid. Initial substances: 2.8 g (1 mole) of p-methyloxanilic ester, 15 g (5 moles) of o-iodotoluene and 1.6 g of magnesium. Yield 4.5 g, or 93.6% of theoretical.

The toluidide dissolves well in ether, benzene, and carbon tetrachloride, poorly in alcohol and acetic acid. It crystallizes from alcohol as colorless lenses melting at 138.5°. In concentrated sulfuric acid it gives a very transient cherry-red coloration.

0.3386 g substance: 20.8 ml 0.05 N H_2SO_4. Found %: N 4.29. $C_{23}H_{23}O_2N$. Calculated %: N 4.06.

p-Phenetidide of o,o-ditolylglycolic acid. 3.6 g (1 mole) of p-ethoxyoxanilic ester, 15 g (5 moles) of o-iodotoluene, and 1.6 g of magnesium were allowed to react together. 4.36 g of substance, or 76.3% of theory, was obtained. On crystallization from alcohol colorless pyramids, melting at 151.5°, were obtained. In concen-

trated sulfuric acid it gives a very transient cherry-red coloration.

0.3120 g substance: 17.5 ml 0.05 N H_2SO_4. Found %: N 3.93. $C_{24}H_{25}O_3N$. Calculated %: N 3.73.

β-Naphthalide of o,o-ditolylglycolic acid. Original mixture was: 6.3 g (1 mole) β-naphthyloxamic ester, 28.2 g (5 moles) of o-iodotoluene, and 3.1 g of magnesium. Colorless rods (from glacial acetic acid) melting at 137-138°. The yield was 8.95 g, or 89.5% of theoretical.

This also gave a transient cherry-red coloration with concentrated sulfuric acid.

0.4224 g substance: 22.01 ml 0.05 N H_2SO_4; 0.3168 g substance: 16.1 ml 0.05 N H_2SO_4. Found %: N 3.64, 3.56. $C_{26}H_{23}O_2N$. Calculated %: N 3.67.

3,3-Di-(o)-tolyloxindole (o-tolylisatin). Concentrated sulfuric acid was added to a solution of 1 g of anilide of o,o-ditolylglycolic acid in 10 ml of glacial acetic acid, until the appearance of the transient cherry red coloration ceased. 0.9 g of substance was obtained, or 95.7% of theory. It crystallized from glacial acetic acid in colorless rods, bunched together in nodules, and melted at 296-297°.

0.1715 g substance: 0.5296 g CO_2; 0.0901 g H_2O; 0.3502 g substance: 11 ml 0.1 N H_2SO_4. Found %: C 84.27; H 5.88; N 4.43. $C_{22}H_{19}ON$. Calculated %: C 84.34; H 6.07; N 4.44.

3,3-Di-(o)-tolyl-5-methyloxindole. This was obtained by condensing the p-toluidide of o,o-ditolylglycolic acid; the yield was 96.8% of theoretical. On crystallization from glacial acetic acid, colorless needles, bunched together into nodules, were obtained. M.p. 296-297°.

0.1543 g substance: 4.3 ml 0.1 N H_2SO_4. Found %: N 3.9. $C_{23}H_{21}ON$. Calculated %: N 4.0.

3,3-Di-(o)-tolyl-5-ethoxyoxindole. This was obtained by condensing the p-phenetidide of o,o-ditolylglycolic acid; the yield was 91.5% of theoretical. The condensation product dissolved well in chloroform, dichloroethane, toluene, and benzene. It crystallized from dichloroethane in colorless platelets, m.p. 285°.

0.1540 g substance: 4.4 ml 0.1 N H_2SO_4. Found %: N 4. $C_{24}H_{23}O_2N$. Calculated %: N 3.97.

3,3-Di-(o)-tolyl-4,5-benzoxindole (3,3-di-(o)-tolyl-β-naphthoxindole). By condensing 1 g of the β-naphthalide of o,o-ditolylglycolic acid, 0.88 g of substance was obtained, which is 92.6% of theory. The condensation product dissolved well in benzene, chloroform, and acetic acid. It crystallized from acetic acid in needles, bunched together into nodules. M.p. 300°.

0.2703 g substance: 7 ml 0.1 N H_2SO_4. Found %: N 3.62. $C_{26}H_{21}ON$. Calculated %: N 3.86.

3,3-Di-(o)-tolyl-6,7-benzoxindole. (3,3-di-(o)-tolyl-α-naphthoxindole). The product of the interaction of 6.8 g (1 mole) of α-naphthyloxamic ester with magnesium iodo-o-toluene (4.5 moles), obtained from 24.5 g of o-iodotoluene and 2.7 g of magnesium, was dissolved in 35 ml of glacial acetic acid. Concentrated sulfuric acid was added to the solution until the appearance of the transient coloration ceased. The condensation product was separated in the usual manner. 7.5 g of air-dry product, or 73.5% of theoretical, was obtained, the yield being calculated on the α-naphthyloxamic ester reacted.

3,3-Di-(o)-tolyl-α-naphthoxindole does not dissolve in water; it dissolves well in ethyl acetate and, on heating, in alcohol and acetic acid.

Colorless needles (from acetic acid) melting at 254°.

0.1645 g substance: 4.6 ml 0.1 N H_2SO_4; 0.1976 g substance: 5.6 ml 0.1 N H_2SO_4. Found %: N 3.81, 3.97. $C_{28}H_{21}ON$. Calculated %: N 3.86.

SUMMARY

1. A method for obtaining o-tolylisatin and its derivatives has been worked out. A series of compounds which has not been previously described in the literature has thus been obtained, and their properties studied.

2. In contrast to the established methods for the preparation of 3,3-diaryl derivatives of oxindole, the intramolecular condensation of aryl amides of α-hydroxycarboxylic acids opens up the possibility of preparing products with any position of the substituent in the aryl groups.

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STUDY OF SULFONATION

XIX. PREPARATION OF 1,3,5-NAPHTHALENETRISULFO CHLORIDE

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By acting on naphthalene with oleum, Gurke and Rudolph [1] first obtained a trisulfo acid of naphthalene, but they did not determine its structure. At 180° a quantity of oleum containing 3.07 moles of free anhydride per mole of naphthalene was introduced, and at 100°, a quantity containing 3.8 moles of anhydride per mole of naphthalene. Later [2], by sulfonating the sodium salt of naphthalene 1,5-disulfo acid at 140° with oleum containing 1.3 moles of free anhydride per mole of sodium salt, or with chlorosulfonic acid at 160°, the 1,3,5-trisulfo acid was obtained, which was characterized by converting it to the trisulfo chloride, with an m.p. of 145-146°. Almost simultaneously the preparation of this 1,3,5-acid was described in French Patent 237,086. It was proposed [3] to obtain the 1,3,5-sulfo acid by the action of 1.25 parts of 70% oleum on 1 part of sodium naphthalenedisulfonate, mixed with 0.5 parts of sulfuric acid monohydrate at 80-90°. Erdman [4] also obtained the 1,3,5-acid from the sodium 1,5-disulfonate at temperatures not exceeding 90°, by sulfonation with oleum containing nearly 4 moles of free anhydride per mole of salt. Busse, Bregman, and Tokhimskaya [5] found that by extending the sulfonation (for 15 hours) by Erdman's method, considerable quantities of a tetrasulfo acid could be produced, instead of the 1,3,5- acid, if oleum containing 3.3 moles of anhydride per mole of the 1,5-disulfo acid salt was used. None of the investigators reported the yield of 1,3,5- acid, except Vorozhtsova and Chuksenova [7], who said, briefly, that "We managed to find a method for preparing 1,3,5-naphthalenetrisulfo acid by the preliminary formation of the α-sulfo acid (sulfonation with sulfuric acid monohydrate at 60°) and the subsequent treatment of the mass with 65% oleum, containing 3 moles of anhydride per mole of naphthalene at 155°. The yield of trisulfo chloride was 70%".

Thus chlorosulfonic acid has never been used as a sulfonating agent for the preparation of 1,3,5-naphthalenetrisulfo chloride, and it has also not been used to obtain acid chlorides of the other naphthalenetrisulfo acids. There is likewise no information about whether the 1,3,5-trisulfo acid was obtained free from other isomeric sulfo acids. In all probability, the formation of the 1,3,5- acid was accompanied by the formation of some of the other isomers.

In the present investigation we have studied the preparation of 1,3,5-naphthalenetrisulfo chloride by the action of chlorosulfonic acid on 1,5-naphthalenedisulfo chloride. It was discovered that if the initial material is pure 1,5-disulfo chloride, decantation of the reaction mass onto ice yields absolutely pure 1,3,5-trisulfo chloride, without any need for further purification.

The results of a series of experiments, set forth in Table 1, show that sulfonation proceeds at 77-78°, and that 6 hours heating of the chloride with large excess of chlorosulfonic acid (50 moles) suffices to produce a trisulfo chloride whose m.p. corresponds to that of the pure compound (146°). For these experiments chlorosulfonic acid, vacuum distilled and containing 97.7% of HSO_3Cl and 2.3% of H_2SO_4, was used. (See Table 1).

At 100° the reaction is completed in 1 hour with 24 moles of chlorosulfonic acid, or in 4 hours with 12 moles. At higher temperatures the reaction is faster, but its rate depends strongly on the amount by which the chlorosulfonic acid is in excess. Comparison of the results of Experiments Nos. 402 and 461 shows that the dichloride is completely sulfonated by 24 moles of chlorosulfonic acid in 1 hour at

Table 1

Action of Vacuum-Redistilled Chlorosulfonic Acid on 1,5-Naphthalenedisulfo Chloride at Various Temperatures

Experiment No.	Taken			Reaction temperature	Duration (hours)	Yield of 1,3,5-trichloride (in % of theoretical)	M.p. of the trichloride obtained
	1,5-Dichloride (in g)	Chlorosulfonic acid (in g)	Chlorosulfonic acid moles/mole of dichloride				
41	1.000	5.350	14.9	78°	3	88.4	131-138°
455	~0.2	~3.3	~50	77	6	--	145-146
461	2.014	17.47	24.0	100	1	85.8	144-145
464	0.750	3.283	12.2	100	4	85.2	146
459	2.000	17.55	24.5	100	6	84.0	145-146
402	1.001	1.78	5.0	125	2	75.8	137-142
452	1.023	3.321	9.1	139	2	82.4	144.5-145
460	0.501	3.33	18.6	146	20 min.	83.6	145-146
24	2.004	1.692	2.35	149	0.5	59.5	127-134

100°, whereas when there are only 5 moles of chlorosulfonic acid, the sulfonation is incomplete even after heating for 2 hours at 125°, as the m.p. of the product obtained shows. A similar conclusion can be reached by comparing the results of the last two experiments (Nos. 460 and 24).

The experimental results set forth in Table 1 also show that even when very large excesses of chlorosulfonic acid are used, ranging from 9-24 moles/mole of 1,5-dichloride, high yields of the 1,3,5-trichloride cannot be obtained. The yields fluctuate between 82.4 and 85.8% of theoretical.

Among various examples of sulfonation with chlorosulfonic acid in the literature, we found no reference to the composition of the acid used. In the majority of cases, nothing at all is said about the nature of the chlorosulfonic acid, and only on extremely rare occasions is reference made to the use of redistilled acid. In the present work it was noted that different samples of chlorosulfonic acid gave different results. The results of experiments with 5 moles of technical acid and with the same acid redistilled one to three times, are set forth in Table 2; they show that a single distillation changes the sulfonating efficiency of chlorosulfonic acid very considerably. With acids distilled two and three times, still higher yields of the trisulfo chloride are obtained.

Table 2

Chlorosulfonation of 1,5-naphthalenedisulfo chloride at 125° C.

Experiment No.	Nature of chlorosulfonic acid	Moles of HSO_3Cl per mole of dichloride	Time of heating (hours)	Trichloride yield (% of theoretical)	M.p. of product obtained
419	Technical	4.75	3	52.3	142-144°
427	Redistilled once	4.87	3	68.7	143-145
421	Redistilled once	5.04	3	69.5	143-145
397	Redistilled once	5	6	69.7	144-146
399	Redistilled twice	5	4	74.6	143-145
405	Redistilled 3 times	4.95	3	75.8	143-145.5
406	Redistilled 3 times	4.87	3	76.1	143-145

In table 3 will be found the results of sulfonations with chlorosulfonic acid; this acid was distilled and then analyzed for chlorine by Volhardt's method, and by titration with alkali. Vacuum-redistilled acid contained, according to the alkali titration, 2.3% of sulfuric acid. In each successive distillation at atmospheric

pressure, the content of highly chlorinated sulfuric acid derivative in the chlorosulfonic acid increased. This derivative was probably either pyrosulfuryl chloride $S_2O_5Cl_2$, or sulfuryl chloride, since the equivalent weight diminished with each distillation.

Table 3

Chlorosulfonation of 1,5-naphthalenedisulfo chloride at 125° for 3 hours

Exp. No.	Nature of Chlorosulfonic acid	Moles of HSO_3Cl per mole of dichloride	Trichloride yield (% of theoretical)	M.p.of trichloride obtained	Equivalent weight of the chlorosulfonic acid by analysis	
					by titration with 0.1 N alkali	by Volhardt titration
465	Redistilled in vacuum	16.9	85.0	145.5-146°	39.08	--
29	Redistilled once	16.6	89.9	145.5-146	39.09	116.3
31	Redistilled twice	14.9	93.9	145.5-146	38.77	113.9
33	Redistilled 3 times	14.6	94.3	145.5-146	38.59	108.8
Calculated for: chlorosulfonic acid HSO_3Cl					38.84	116.53
	pyrosulfuryl chloride $S_2O_5Cl_2$				35.84	107.53
	sulfuryl chloride SO_2Cl_2				33.75	67.50

At the same time, the larger the content of the more highly chlorinated derivative in the chlorosulfonic acid, the larger was the yield of trisulfo chloride in the sulfonation, in spite of some decrease in the excess of chlorosulfonic acid used.

The next experiments demonstrated how an acid having higher content of high chlorine derivative, and better sulfonating efficiency, can be obtained: either as a result of prolonged boiling with repeated distillation, or by fractional separation of the chlorine-containing substance from sulfuric acid.

About 50 ml of chlorosulfonic acid, redistilled at atmospheric pressure, was heated for 12 hours at a liquid temperature of 139-149°. From this about 21 ml of liquid distilled off, which in distillation gave 10 ml of a fraction boiling over the range 68-70°. Titration of this fraction by Volhardt's method, and with 0.1 N alkali, gave the following results:

0.0930 g substance: 27.01 ml 0.1 N NaOH; 13.78 ml 0.1 N $AgNO_3$. 0.1024 g substance: 29.75 ml 0.1 N NaOH. Found: NaOH equivalent 34.43, 34.46, equivalent $AgNO_3$ 67.41, SO_2Cl_2. Calculated: equivalent NaOH 33.75, equivalent $AgNO_3$ 67.50.

These results show that the substance is sulfuryl chloride. A portion of the heated chlorosulfonic acid was distilled. For the following experiments acid which had been both heated and distilled, and acid which had merely been heated, was used. The results of the first two experiments, given in Table 4, show that the heated acid gives considerably less trisulfo chloride on sulfonation, than it does after a double distillation. The following two pairs of experiments in Table 4 demonstrate that the normal technical acid, whether heated prior to distillation, or when distilled without prior heating, gives practically identical yields of trisulfochloride.

Table 4 - Chlorosulfonation

of 1,5-Naphthalenedisulfo Chloride with Chlorosulfonic Acid at 125° for 3 Hours

Exp. No.	Nature of chlorosulfonic acid	Moles of HSO_3Cl per mole of dichloride	Trichloride yield (% of theoretical)	M.p.of trichloride obtained
50	Heated 12 hrs without distillation	10	69.1	145.5-146°
400	Redistilled 2 times	10	88.4	145
58	Heated 12 hrs, 1 dist.	5	68.7	144-145.5
429	Redistilled once	4.95	69.2	143-144
53	Heated 12 hrs, 1 dist.	14.9	92.0	145.5-146
425	Redistilled once	14.5	93.1	144-146

Thus, although a high-chlorine derivative of sulfuric acid is formed in the acid by heating, the sulfuric acid concentration rises simultaneously, and a chlorosulfonic acid with a lowered sulfur content and with more of the high-chlorine derivative can only be obtained by fractionation, which results in a separation of the sulfuric acid. It may be suggested that the high-chlorine derivative, which increases the yield of trisulfo chloride, is either sulfuryl chloride or pyrosulfuryl chloride. In Table 5

are set forth the results of experiments on sulfonation with chlorosulfonic acid to which sulfuryl chloride or phosphorus pentoxide had been added, the latter addition being based on the known fact that when chlorosulfonic acid is heated with phosphorus pentoxide, pyrosulfuryl chloride is obtained. The results of the first four experiments show that sulfuryl chloride does not increase the yield of trichloride, whereas the last five show that the yield is increased when phosphorus pentoxide is present.

Table 5

Chlorosulfonation of 1,5-Naphthalenedisulfo Chloride with Additions of Sulfuryl Chloride and of Phosphorus Pentoxide

Exp. No.	Amount taken: Chlorosulfonic acid: Nature	Amount taken: Chlorosulfonic acid: Moles per mole of dichloride	SO_2Cl_2 moles/mole of dichloride	P_2O_5 moles/mole of dichloride	Reaction temperature	Duration (hours)	Yield of dichloride (in % of theoretical)	M.p. of trichloride obtained
400	Distilled twice	10	--	--	125°	3	88.4	145°
39	Distilled once	10.1	3.86	--	78 and 125	1/2	87.1	145.5-146
40	Distilled once	10.1	3.68	--	78 and 125	1/6	85.4	145.5-146
42	Distilled once	10.1	1.93	--	125 and 146	1/2	85.2	145.5-146
43	Distilled once	9.9	--	1.36	125	3	94.9	145-145.5
47	Distilled 3 times	10.1	--	0.90	125	3	94.7	141.5-143.5
54	Distilled 3 "	10.0	--	0.76	125	3	94.8	145-145.5
70	Distilled 3 "	4.6	--	0.48	150	3	87.9	141.5-142
57	Distilled 3 "	5.1	--	--	125	3	74.8	144-145

It follows, from all that has been said, that the presence of sulfuric acid in chlorosulfonic acid lowers the yield of trichloride. The presence of sulfuryl chloride has no influence on the yield. The presence of phosphorus pentoxide, which produces pyrosulfuryl chloride in the chlorosulfonic acid, increases the yield of trichloride, but on the other hand decreases the rate of chlorosulfonation.

In Table 1 the result of certain experiments in which a large excess of vacuum-distilled chlorosulfonic was used, show that it is not possible to reach a yield of trichloride higher than 86% of theory. In Table 6 are set forth the results of experiments on chlorosulfonation with a large excess of chlorosulfonic acid, distilled at atmospheric pressure, which show that it is possible to get a nearly quantitative yield (97.7% of theoretical).

Table 6

Chlorosulfonation of 1,5-Naphthalenedisulfo Chloride at 125° for 3 Hours

Exp. No.	Chlorosulfonic acid: Nature	Moles/mole of dichloride	Trichloride yield (in % of theoretical)	M.p. of trichloride obtained
428	Distilled once	24.1	96.0	145-146°
430	Distilled 3 times	47.6	96.4	145-146
38	Distilled 3 times	24.3	97.7	145.5-146

NOTE: In each experiment a different sample of chlorosulfonic acid was used.

Thus even a very small quantity of sulfuric acid in chlorosulfonic acid lowers the yield of the trichloride markedly.

EXPERIMENTAL

For this work the 1,5-naphthalenedisulfo chloride, melting at 183° or 184°, was used. The chlorosulfonic acid was distilled from Wurtz flasks with fused-on condensers. The thermometer was suspended in the liquid from a wire which passed through the reflux air condenser; the latter fitted into a ground joint in the neck of the flask. Technical chlorosulfonic acid was distilled in vacuum at a pressure of 15-20 mm, and at 70-80°. When distilling under atmospheric pressure, the first small fraction, boiling at 143-147°, was rejected. During the subsequent distillation, the results of analyses of samples from which are set forth in Table 3, fractions were withdrawn within certain temperature limits: when distilling once, 151-157°, when distilling twice, 146-153°, and when distilling three times, 143-152°. At the end of distillation a considerable amount of acid always remained in the flask.

The chlorosulfonation was conducted in a flask having a reflux air condenser fitted to it in a ground joint; the flask was heated in an Eichmann apparatus [9]. The reaction mass was decanted onto ice. After standing overnight the trichloride was filtered off, washed, dried, and weighed. After this its m.p. was determined.

SUMMARY

By chlorosulfonating 1,5-naphthalenedisulfo chloride with chlorosulfonic acid, pure 1,3,5-trisulfo chloride was obtained in yield of up to 97.7% of the theoretical, when a large excess of chlorosulfonic acid, which had been distilled more than once, was used.

When vacuum-distilled chlorosulfonic acid was used, containing 2.3% of sulfuric acid, the yield, even with a large excess of acid, did not exceed 85%, as a result of the conversion of the trisulfo chloride to the trisulfo acid.

Technical (93%) chlorosulfonic acid gives, in contrast to distilled acid, a low yield of trichloride.

When chlorosulfonic acid is distilled, a small quantity of sulfuryl chloride and, apparently, of pyrosulfuryl chloride, is formed. The latter impurity increases the yield of the chlorosulfonation product.

Chlorosulfonation with chlorosulfonic acid containing added P_2O_5 increases the yield of trichloride.

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HYDROLYSIS OF 4,4'-DINITRODIPHENYLCARBAMIDE (4,4'-DINITROCARBANILIDE)

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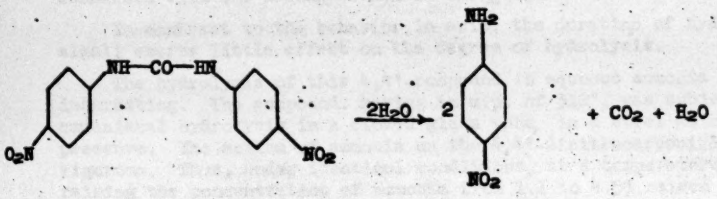
There has been very little study of the hydrolysis of substituted carbanilides. Gershzon and Lastovsky found, when studying the aryl derivatives of urea, that diphenyl urea and di-o-tolyl urea are only very weakly hydrolized in acids. On the other hand, di-o-tolyl urea, which is scarcely affected by treatment with acid or alkali at normal pressure, is almost completely hydrolyzed by acids at elevated pressures [1]. Ostrozhinskaya and Kozlova found that sulfo-containing derivatives of carbanilide hydrolyze easily and, for example, urea-I-acid (5,5'-dihydroxy-7,7'-disulfo acid-2,2'-dinaphthylurea) is 25% hydrolyzed when heated for an hour in a solution of sodium carbonate [2]. At the same time there is information according to which the hydrolysis of carbanilide and its substituted derivatives proceeds more readily only in aqueous ammonia [3].

Special interest is attached to the hydrolysis of substituted carbanilides, and to that of 4,4'-dinitrocarbanilides in particular, since such compounds may find practical application in the production of aromatic nitroamides and their derivatives. The hydrolysis in the case under discussion is represented as follows:



Study of the hydrolysis of 4,4'-dinitrocarbanilide in sulfuric acid showed that the yield of p-nitroaniline increased as the concentration of the acid increased. The optimum concentration was 74.8% sulfuric acid, the yield here being 97.45%. Further elevation of the concentration lowered the yield of the p-nitroaniline.

Analagous effects are observed when the temperature of hydrolysis is changed. While at 150° the yield is 96.74%, at 175° it falls to 71%.

It was found that the effect of extending the duration of hydrolysis from ½ hour to 1 hour was to increase the yield from 58.4 to 98.8%.

The findings relative to hydrolysis with sulfuric acid apply with small deviation also to the hydrolysis of 4,4'-dinitrocarbanilide with hydrochloric acid. Thus 4,4'-dinitrocarbanilide is not hydrolyzed, whatever the concentration of the hydrochloric acid, if the temperature is below 100°. Elevation of the temperature causes a rapid increase in the yield of p-nitroaniline: while the yield is only 25.33% at 105°, at 180° it reaches 65.93%. Extending the duration of hydrolysis and changing the concentration of the hydrochloric acid produce approximately the same effects on the yield of p-nitroaniline as in hydrolysis with sulfuric acid. Increasing the duration of hydrolysis from 0.5 to 12 hours raises the yield from 8.24 to 90.02%. Increasing the concentration of acid from 34 to 36.6% increases the yield from 82.81 to 92.26%.

When the facts described above are compared with the conditions for hydrolysis of unsubstituted carbanilides, it must be admitted that more severe conditions are required to achieve the hydrolysis of the substituted compounds, on account of the presence of two electronophilic nitro groups in the carbanilide molecule. At the same time the general dependence of the process on the conditions of reaction (such as raising the temperature, increasing the time of heating, changing the concentration of the acid) remain the same in both cases. It is of practical interest that the molecule of dinitrodiphenylurea does not split up at temperatures below 100°, whatever the concentration of the acid: this presents a method for purifying this compound (and possibly many other substituted ureas) by treatment with acid at temperatures of up to 100°.

The hydrolysis of the 4,4'-compound in alkalies is of equal interest. In such a medium (10% NaOH) the hydrolysis likewise does not proceed at all at temperatures below 100°. In these conditions the 4,4'-compound is just as stable in alkali as in acid. Raising the temperature raises the degree of hydrolysis markedly and with it the yield of p-nitroaniline. While the yield of this compound is 3.02% at 100°, it is 73.25% of theory at 150°.

Changing the concentration of the alkali exerts a stronger influence on the hydrolysis than does changing the acid concentration. In 0.5% NaOH, the yield of p-nitroaniline is 30.07% in 1% solution it is 74%. However, further elevation of the alkali concentration lowers the yield, which is connected with the decomposition of the p-nitroaniline in the alkali.

In contrast to the behavior in acid, the duration of hydrolysis in alkali exerts little effect on the degree of hydrolysis.

The hydrolysis of this 4,4'-compound in aqueous ammonia is extremely interesting. The compound, having an m.p. of 312°, was subjected to ammoniacal hydrolysis in a closed glass tube, in a steel autoclave under pressure. The action of ammonia on the 4,4'-dinitrocarbonilide was usually vigorous. Thus, under identical conditions, at a temperature of 150°, raising the concentration of ammonia from 1.1 to 4.5% raised the yield of p-nitroaniline from 58.74% to 92.58%. At 125°, raising the ammonia concentration from 4.5 to 20% raised the yield from 14.34 to 95.50% of theory. Consequently, it was possible to hydrolyze 4,4'-dinitrocarbanilide at much lower temperatures, but using a higher ammonia concentration.

It must be mentioned that the yield of p-nitroaniline was found to depend on the duration of the treatment. By decreasing the time the yield was decreased. Extension of the time of hydrolysis in aqueous ammonia had nearly the same effect on the yield as it had when using hydrochloric acid, but this effect was in no way similar to the effect in aqueous caustic soda.

On the basis of what has been reported above, it may be assumed that the best hydrolytic agent for 4,4'-dinitrocarbanilide is an aqueous ammonia solution: as it is present in small concentration, it ensures almost complete hydrolysis of the original substance; the p-nitroaniline has a melting point very near to 146-147°, reported for it in the literature.

EXPERIMENTAL

1) Hydrolysis of 4,4'-dinitrocarbanilide in 56.1% sulfuric acid at 150°. 1.052 g of 4,4'-dinitrocarbanilide, melting at 312°, was placed in a flask equipped with a reflux air condenser and a thermometer. Into this flask was introduced 10 g of 60.1% sulfuric acid, and the mixture was heated at 150° for 3.5 hours. After cooling, the mass was decanted on to 50 g of ice in 100 ml of water, and the p-nitroaniline was diazotized with a sodium nitrite solution. The yield of p-nitroaniline was 81.15%.

Effect of concentration on the yield of p-nitroaniline during hydrolysis with sulfuric acid. The hydrolysis was conducted at 150° with 10 g of sulfuric acid at different concentrations. The duration of reaction was 1 hour. The quantity of p-nitroaniline was determined by titration in the reaction mass. The results are in Table 1.

Table 1

Expt. No.	Quantity of 4,4'-dinitrocarbanilide, g	H_2SO_4 Concentration (%)	Yield of p-nitroaniline (in %)
1	1.0514	56.10	73.45
2	1.0508	64.98	91.41
3	1.0460	74.80	97.45
4	1.0220	79.60	94.23
5	1.0650	85.00	91.88

Table 2

Expt. No.	Quantity of 4,4'-dinitrocarbanilide, g	Temperature	Yield of p-nitroaniline (in %)
1	1.0500	125°	9.70
2	1.0488	150	96.74
3	1.0500	175	71.00

Influence of temperature on the yield of p-nitroaniline in hydrolysis with sulfuric acid. The concentration of sulfuric acid, in all cases, was kept at 74.8%. The results are set forth in Table 2.

Influence of duration of heating on the yield of p-nitroaniline in hydrolysis with sulfuric acid. The acid concentration was 74.8%, the quantity 10 g in all cases, the temperature 150°. The results are set forth in Table 3.

Table 3

Expt. No.	Quantity of 4,4'-dinitrocarbanilide (in g)	Duration of heating (in hours)	Yield of p-nitroaniline (in %)
1	1.0532	0.25	58.40
2	1.0504	0.5	79.3
3	0.0540	0.75	90.10
4	1.0460	1	98.80
5	1.0512	1.25	97.56
6	1.0508	1.5	93.30

2) Hydrolysis of 4,4'-dinitrocarbanilide with 34% hydrochloric acid at 100°. 1.05 g of the 4,4'-compound was heated with 20 g of HCl in a flask provided with reflux condensation. The mixture was heated at 100° for 1 hour on an oil bath. After cooling the mixture was diazotized: an appreciable quantity of the nitrite remained unused.

Influence of temperature on the yield of p-nitroaniline in the hydrolysis of the 4,4'-compound with hydrochloric acid. Concentration of HCl 34%, quantity 10 g, duration of process 6 hours. The reactants were contained in a sealed glass tube, which was heated for six hours after closure. The contents of the tube were then titrated with 0.1 N nitrite, and the yield of p-nitroaniline determined. The results are set forth in Table 4.

Influence of the duration of hydrolysis on the yield of p-nitroaniline when using hydrochloric acid. Concentration of acid 35.9%, quantity 10 g, temperature 150°. Results in Table 5.

Table 4

Expt. No.	Quantity of 4,4'-dinitrocarbanilide (in g)	Temperature	Yield of p-nitroaniline (in %)
1	0.5170	105°	25.33
2	0.5356	125	43.15
3	0.5156	150	65.93
4	0.5048	170	82.81
5[1]	0.5077	170	92.26

Table 5

Expt. No.	Quantity of 4,4'-dinitrocarbanilide (in g)	Duration (in hours)	Yield of p-nitroaniline (in %)
1	0.5304	0.5	8.24
2	0.5109	1	20.25
3	0.5084	2.5	44.80
4	0.5242	5	74.69
5	0.5566	6	81.76
6	0.5220	8	88.28
7	0.5264	10	89.85
8	0.5138	12	90.02

3) Hydrolysis of 4,4'-dinitrocarbanilide in caustic soda at 100°. 1 g of the 4,4'-compound was introduced into a flask with 12 g of 10% NaOH. The mixture was heated at 100° for 6 hours. After cooling, the mixture was neutralized with hydrochloric acid, leaving the mixture finally acid. It was diazotized with 0.1 N sodium nitrite. 0.4 ml of nitrite was used. The yield of p-nitroaniline was 3.02%.

Effect of temperature, alkali concentration and duration of heating on the yield of p-nitroaniline during hydrolysis with aqueous sodium hydroxide. In all experiments the quantity of 4,4'-compound was 10 g, and of alkali 150 g; the reaction was carried out in a steel autoclave with a stirrer and heated over an oil bath. The experimental results are set forth in Table 6.

Table 6

Expt. No.	Alkali Concentration (in %)	Temperature	Duration of hydrolysis (hrs)	Yield of p-nitroaniline (%)	M.p. of p-nitroaniline
1	1	105°	6	-	-
2	1	125	6	35.05	132.5°
3	1	150	6	79.27	140
4	1	170	6	58.05	132.5
5	0.5	150	6	90.07	137.5
6	1	150	6	74.00	142.5
7	5	150	6	38.33	132.5
8	10	150	6	5.48	130.5
9	1	150	1	64.62	137
10	1	150	3	77.21	138.5
11	1	150	6	74.48	138
12	1	150	9	72.29	138

4) Hydrolysis of 4,4'-dinitrocarbanilide with aqueous ammonia. 1.054 g of the 4,4'-compound and 10 g of a 1.1% solution of aqueous ammonia were introduced into a tube which was then sealed off. It was heated for 8 hours at 150°. The contents of the tube were transferred to a beaker, acidified with 10% HCl, and titrated with 0.5 N $NaNO_2$. The yield of p-nitroaniline was 56.74%.

[1] In Expt. No. 5 the concentration of HCl was 35.6%.

Influence of the aqueous ammonia concentration on the yield of p-nitroaniline in the hydrolysis of the 4,4'-compound. 10 g of the compound was heated in a steel autoclave with 150 g of aqueous ammonia. The maximum pressure in the autoclave was 7-8 atm. At the end of a specific time the autoclave was cooled. After the product had been discharged its amount and m.p. were determined. The results are set forth in Table 7.

Table 7

Expt. No.	Quantity of 4,4'-dinitrocarbanilide (in g)	Quantity of ammonia (in g)	Concentration of ammonia (in %)	Duration of process (hours)	Temperature	Yield of p-nitroaniline (in %)
			In sealed glass tube			
1	1.0540	10	1.10	8	150°	58.74
2	0.0492	10	1.88	8	150	79.33
3	1.0562	10	2.10	8	150	83.61
4	1.0510	10	4.5	8	150	92.58
			In steel autoclave			
5	10	150	4.5	5	125	14.34
6	10	150	10	5	125	49.29
7	10	150	15	5	125	79.96
8	10	150	20	5	125	95.50

Influence of the duration of the process on the yield of p-nitroaniline in hydrolysis with aqueous ammonia. The experiments were carried out in an autoclave; the quantity of 4,4'-dinitrocarbanilide was 10 g, and of ammonia 150 g, the concentration of ammonia was 4.5%, and the temperature was 150°. The results are in Table 8.

Table 8

Expt. No.	Duration of Reaction (hours)	Yield of p-nitroaniline (%)	M.p. of p-nitroaniline
1	0.5	4.38	147°
2	1	50.38	147
3	2	76.67	147
4	3	86.65	146
5	4	89.76	145
6	5	93.21	146.5

SUMMARY

1. The hydrolysis of 4,4'-dinitrocarbanilide in the presence of acid is incomplete.

2. The hydrolysis is likewise incomplete in caustic alkali. In this case, apparently, there is a simultaneous breakdown of the p-nitroaniline, which is the product of hydrolysis.

3. The best hydrolytic agent for 4,4'-dinitrocarbanilide is aqueous ammonia: this produced the most complete hydrolysis of the initial material, giving p-nitroaniline in high yield and good quality.

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SYNTHESIS OF DERIVATIVES OF 1-HYDROXYPHENAZINE

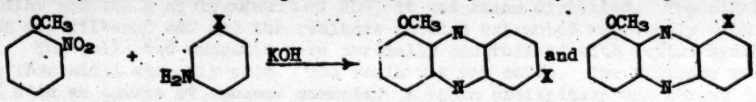
II. 1,6- and 1,8-DIALKOXYPHENAZINES

S. B. Serebryanyi and V. P. Chernetsky

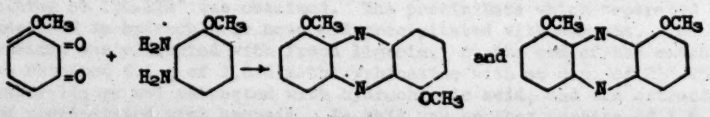
Of the ten possible isomeric dimethoxyphenazines we obtained earlier the 1,5- and 1,7- isomers [1]. Five isomers (1,2-, 2,3-, 1,4-, 3,6-, and 2,6-) have been described by other authors [2-5]. At the end of 1946 Clemo and Dsglish [6] reported the synthesis of a mixture of the 1,5- and 1,8- isomers, and stated that they had separated the mixture chromatographically, obtaining thereby two dimethoxyphenazines melting at 245-246° and 253-254°. However, they were unable to decide which of the two compounds was the 1,5- and which the 1,8-. Thus, at present, the 1,3- and 1,6- compounds have not been obtained and although the 1,8- compound has been obtained it has not been characterized.

In the present communication the synthesis and separation of 1,6- and 1,8-dimethoxyphenazines and of the 1,6- and 1,8-diethoxyphenazines are described, and likewise the synthesis and separation of 1,5- and 1,8-dimethoxyphenazines. The synthesis of the two last named compounds made it possible for us to identify all the products described here, and also to decide the question of the structure of iodine [7].

To obtain the 1,6- and 1,8-dialkoxyphenazines we made use of the condensation of aromatic nitro compounds with aromatic amines in the presence of powdered potassium hydroxide, successfully used by us at an earlier date for the synthesis of other phenazine derivatives [1,8]. If this reaction is brought about between o-nitrophenetole or o-nitroanisole and an m-substituted aromatic amine, a mixture of two phenazines, the 1,6- and 1,8- can be produced.



Actually, by reacting o-nitroanisole with m-anisidine, and o-nitrophenetole with m-phenetidine, we obtained a mixture of the 1,6- and 1,8-dimethoxyphenazines in the first case and a mixture of the 1,6- and 1,8-diethoxyphenazines in the second. We worked out a method of separating the 1,6- and 1,8-dialkoxyphenazines, based upon their different solubilities in ligroin, alcohol, and acetic anhydride. 4 derivatives were obtained (I-IV): two dimethoxyphenazines, I melting at 174°, and II melting at 259-260°; and two diethoxyphenazines: III melting at 153° and IV melting at 174°. (These melting points and those given later on are uncorrected). We succeeded in establishing the position of the methoxy group in compounds I and II as follows. We obtained earlier the 1,5- isomer melting at 249-250° [1]. We accordingly condensed 3-methoxy-o-benzoquinone with 3-methoxy-o-phenylenediamine according to the scheme:



and in this way obtained two products, one of which should be, according to the above equation, the 1,5-dimethoxyphenazine already known to us, and the other the 1,8-dimethoxyphenazine.

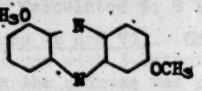
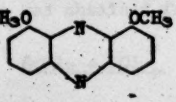
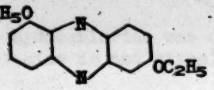
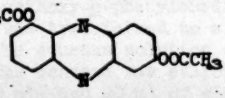
We separated the two compounds from the mixture with picric acid, since we already knew that 1,5-dimethoxyphenazine does not form a picrate in alcoholic solution, whereas the compounds I and II, one of which ought to be the 1,8- isomer, easily formed picrates in the cold. Treatment of the alcoholic solution of the mixture of 1,5- and 1,8- isomers with picric acid yielded a picrate having an m.p. of 258° (with decomp.). From this picrate we obtained pure dimethoxyphenazine (V) whose m.p. agrees with the m.p. of compound II: 259-260°. There was no depression of the m.p. when these two compounds (V and II) were mixed. From the alcoholic mother liquor, after separation of the picrate of V, we isolated a dimethoxyphenazine (VI) melting at 249-250°. A mixture of the preparation VI with the 1,5-dimethoxyphenazine, isolated earlier, gave no depression of the m.p. It follows from this that: 1) compound VI is 1,5-dimethoxyphenazine; 2) compounds II and V are identical and are therefore 1,8-dimethoxyphenazine; and 3) compound I can only be 1,6-dimethoxyphenazine.

The structure of the diethoxyphenazines III and IV was established by dealkylation with hydrobromic acid, followed by acetylation of the dihydroxyphenazines obtained with acetic anhydride. In this way two diacetoxyphenazines were obtained: VII melting at 148-149°, and VIII with an m.p. of 256-258°. In a similar manner the diacetoxyphenazines were converted to the 1,6- and 1,8-dimethoxyphenazines; 1,6-diacetoxyphenazine melts at 148-149°; and the 1,8-isomer at 256-258°. Mixing 1,6-diacetoxyphenazine with diacetoxyphenazine VII and the 1,8-diacetoxy compound with VIII caused no melting point depression in either case. Consequently compound III must be 1,6- diethoxyphenazine, and IV, 1,8-diethoxyphenazine.

The melting points of all these compounds which we obtained are set out in the table.

EXPERIMENTAL

1,6- and 1,8-dimethoxyphenazines (I) and (II). After allowing the reacting mixture to stand for three days in a covered flask (30 g o-nitroanisole, 30 g m-anisidine and 120 g of dry pulverized KOH) it was steam distilled. The alkaline solution was filtered off and the resinous residue extracted repeatedly with hot 15% HCl. The collected extracts were partially neutralized with sodium hydroxide, leaving them still strongly acid. The resin was set aside. The filtrate was treated with an excess of aqueous ammonia. A brown precipitate was thrown down, which was filtered off, washed with water, and dried. The yield was 5.3 g, m.p. 215-220°. This precipitate was extracted with ligroin in a Soxhlet, the ligroin solution extracted with 15% HCl, and the acid extract treated with an excess of aqueous ammonia. The dried precipitate was again extracted with ligroin in a Soxhlet. 1,6-Dimethoxyphenazine dissolves in ligroin more easily than the 1,8-isomer, hence in the first 12 hours of extraction the former was completely dissolved and only small quantities of the latter went into solution in the ligroin. Cooling the hot ligroin solution somewhat produced a precipitate consisting of the 1,6-dimethoxyphenazine, contaminated with the 1,8- isomer and some resinous matter. The still hot solution was decanted from the precipitate into a beaker, and on cooling nearly pure 1,6-dimethoxyphenazine crystallized out. This was filtered off, washed with ligroin and purified by precipitation from its solution in HCl with NH_3. In this manner 0.5 g of 1,6-dimethoxyphenazine melting at 171-172° was obtained. The precipitate which separated earlier was dissolved in hydrochloric acid and precipitated with ammonia. The substance obtained was extracted with fresh ligroin. At the end of the extraction there was obtained 0.1 g of 1,8-dimethoxyphenazine with an m.p. of 252-253°. The mother liquor was extracted with hydrochloric acid, and the extract neutralized and precipitated with ammonia. In this way another portion of 1,6-dimethoxyphenazine was obtained. To purify this it was crystallized from 6 ml of acetic anhydride.

Compound No.	Description of Compound	Formula	M.p.
I	1,6-dimethoxyphenazine		173°
II and V	1,8-dimethoxyphenazine		259-260
III	1,6-diethoxyphenazine		153
IV	1,8-diethoxyphenazine		174
VII	1,6-diacetoxyphenazine		148-149
VIII	1,8-diacetoxyphenazine		256-258

In this way 0.7 g of the 1,6- isomer was obtained, melting at 169-170°; altogether 1.2 g of the 1,6- isomer.

To extract the 1,8- isomer we utilized the ligroin mother liquor, from which the first portion of the 1,6- isomer had been separated. The extraction and isolation were accomplished as follows. After extracting for 6-8 hours in a Soxhlet the solution obtained was cooled, and a part of the 1,8- isomer crystallized out from it in the form of large brown needles. The mother liquor was decanted into another flask and served for another extraction operation. The precipitate was washed with ligroin and dried. By repeating this operation five times, we isolated 2.7 g of 1,8-dimethoxyphenazine, melting at 253-255°. In all 2.8 g of the isomer was isolated.

For a final purification of the 1,6- isomer (I), it was twice recrystallized from ligroin or acetic anhydride. Small yellow needles, m.p. 175°.

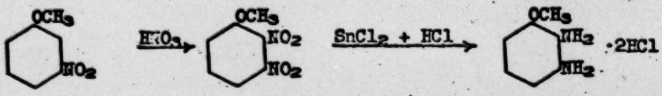
Found %: N 11.57. $C_{14}H_{12}O_2N_2$. Calculated %: N 11.66.

Picrate $C_{14}H_{12}O_2N_2 \cdot C_6H_2(NO_2)_3OH$, orange needles from benzene, m.p. 258° (with decomp.).

1,8-Dimethoxyphenazine (II) was purified via the picrate. To a cold alcoholic solution of the base an alcoholic solution of picric acid was added. After some minutes the picrate separated in the form of dark red needles. The picrate crystallized from alcohol with an m.p. of 258° (with decomp.). (Admixture of the picrate of the 1,6- isomer depressed this m.p. by 20-25°). The free base was regenerated by heating the picrate with 15% hydrochloric acid. The base was filtered off, washed with water to complete the removal of the picric acid, and then crystallized from ligroin. Long, threadlike, bright yellow needles melting at 259-260°.

Found %: N 11.53. $C_{14}H_{12}O_2N_2$. Calculated %: N 11.66.

1,5- and 1,8-Dimethoxyphenazines (V and VI). These compounds were obtained by condensing 3-methoxy-o-benzoquinone with 3-methoxy-o-phenylenediamine. The pyrogallol requisite for obtaining the quinone was prepared according to Hilleman [8]. 3-Methoxy-o-phenylenediamine was obtained from m-nitroanisole thus [10]:



3-Methoxy-o-phenylenediamine hydrochloride was obtained in 60% yield (in the literature the yield of the diamine is not given). It melted at 245-247° (with decomp.).

a) Condensation. 2.5 g of the 1-methyl ether of pyrogallol (boiling at 120-122°/7 mm) in 750 ml of dry benzene was shaken with lead peroxide for 10 minutes. After standing for two minutes the quinone solution was filtered off from the lead peroxide, and the latter washed with 100 ml of benzene. 1.75 g of the hydrochloride of 3-methoxy-o-phenylenediamine was dissolved in 20 ml of water. The solution was transferred to a separating funnel and neutralized with soda ash. The aqueous solution of amine was extracted 6 times with 20 ml of benzene. The benzene was evaporated in vacuum until its volume had been reduced to 40 ml, and 20 ml of glacial acetic acid was added to the solution. This mixture was poured into the benzene solution of the quinone. An immediate change of color was observed. After standing for two hours at room temperature the mixture was transferred to a separating funnel, and washed three times with 50 ml of water, twice with 50 ml of caustic soda, and twice again with water. The benzene solution was considerably clarified by this treatment. After it had been extracted four times with 15% HCl (100 ml), the hydrochloric acid solution was treated with an excess of ammonia. The mixture of 1,5- and 1,8-dimethoxyphenazines was purified by extraction with ligroin in a Soxhlet, followed by treatment of the ligroin solution with hydrochloric acid and precipitation from the latter with ammonia. 1 g of a mixture of the two isomers was obtained, which had an m.p. of 215-220°.

b) Isolation of the isomers. 1 g of the mixture of the 1,5- and 1,8-compounds was dissolved in 200 ml of alchol with heating. To the solution was added a solution of 1 g of picric acid in 25 ml of alcohol. After being kept cool for 10-15 minutes the solution began to deposit crystals of the 1,8-dimethoxyphenazine picrate. The picrate was filtered off, washed with 40 ml of alcohol, and this alcohol added to the mother liquor. The mother liquor was evaporated to 75 ml. From it was separated a further small quantity of picrate. In all, 1.2 g of the picrate of the 1,8- compound was collected, melting at 254° (with decomp.). The 1,8- compound was regenerated from the picrate but the 1,5- compound was isolated from the mother liquor.

1.2 g of the picrate of 1,8-dimethoxyphenazine was heated with 100 ml of 15% hydrochloric acid. The solution of the hydrochloride of the base was filtered and treated with an excess of ammonia. The precipitate of small yellow needles of the base was filtered off and washed with water to complete removal of the picric acid. 0.65 g of the base was obtained, m.p. 254-255°. For a more complete purification, the substance was reconverted to the picrate.

The picrate was filtered off and washed with alcohol. 1.1 g of picrate, melting at 258° (with decomp.) was obtained. From this picrate pure 1,8-dimethoxyphenazine (V) was obtained by decomposition with hydrochloric acid, and subsequent crystallization from ligroin. The compound crystallized in long, threadlike, bright-yellow needles, melting at 259-260°. Admixture with compound II produced no depression of the m.p.

Found %: N 11.37. $C_{14}H_{12}O_2N_2$. Calculated %: N 11.66.

After separation of the picrate of the 1,8- compound, the alcoholic mother liquor from the mixture was evaporated almost to dryness, and was afterwards treated with 30 ml of 15% hydrochloric acid. The solution of the hydrochloride was filtered, diluted to 1 liter with water and allowed to stand overnight.

As a result of hydrolyzing the hydrochloride, the free base separated out. It was collected and recrystallized twice from alcohol. 0.35 g of yellow needles, melting at 249-250°. Admixture with the 1,5- isomer did not depress its m.p.

Found %: N 11.72. $C_{14}H_{12}O_2N_2$. Calculated %: N 11.66.

1,6- and 1,8-Diethoxyphenazines (III and IV). From the action of pulverized potassium hydroxide on 20.6 g of o-nitrophenetole and 20.6 g of m-phenetidine, 7.5 g of a crude mixture melting at 152-166° was obtained. When this was extracted with 300 ml of ligroin, 3.1 g of substance melting at 165-170° crystallized out. These crystals consisted mainly of the 1,8-diethoxyphenazine. By crystallizing it from alcohol 2.8 g was obtained melting at 171-173°. This was practically pure 1,8- isomer. The alcoholic mother liquor was reduced to half its initial volume by distillation. The treatment of the alcoholic mother liquor is described later. The ligroin mother liquor was extracted with hydrochloric acid, and by precipitation with ammonia from the solution of hydrochloride, 3.5 g of a substance melting at 150-157° was obtained. After recrystallizing it from 8 ml of acetic anhydride, 1.3 g of nearly pure 1,6-diethoxyphenazine, melting at 150-151° was obtained. Pure 1,6-diethoxyphenazine was obtained from this preparation by crystallization from 150 ml of ligroin. Yellow needles, 1.1 g melting at 152°. The acetic anhydride from the crystallization of the 1,6- isomer was distilled until its volume had been reduced by two thirds, and was treated with hydrochloric acid. To this solution was added the hydrochloride solution obtained by treating the alcoholic mother liquor with HCl. The combined hydrochloride solutions were filtered and treated with ammonia. The precipitate was collected, dried and extracted with fresh ligroin in a Soxhlet. The 1,8- isomer separated from the solution, leaving behind in the mother liquor a mixture of itself with the 1,6- compound, together with foreign impurities. Repetition of the treatment of the mother liquor with HCl and subsequent extraction with ligroin of the precipitate resulting from the addition of ammonia gave a nearly complete separation of the two isomers, and produced finally 0.3 g of the 1,6- and 0.4 g of the 1,8-compounds. In all 3.2 g of the 1,8- and 1.5 g of the 1,6- diethoxy compounds were obtained.

1,6-Diethoxyphenazine (III) was obtained pure by double recrystallization of the crude product from ligroin or acetic anhydride. Fine yellow needles, melting at 153°.

Found %: N 10.42. $C_{16}H_{16}O_2N_2$. Calculated %: N 10.45.

Picrate $C_{16}H_{16}O_2N_2 \cdot C_6H_2(NO_2)_3OH$ orange needles from alcohol, m.p. 225-226°.

1,8-Diethoxyphenazine (IV) was obtained in the pure state by double recrystallization from ligroin or alcohol. Long yellow needles from ligroin, yellow leaflets from alcohol, m.p. 174°.

Found %: N 10.47. $C_{16}H_{16}O_2N_2$. Calculated %: N 10.45.

Picrate $C_{16}H_{16}O_2N_2 \cdot C_6H_2(NO_2)_3OH$ red needles from benzene, m.p. 253-254° (with decomp.).

Both the 1,6- and the 1,8- isomers dissolve in diluted hydrochloric acid with the formation of salts. The hydrochloric acid solutions of the 1,6-dialkoxyphenazines are orange, and those of the 1,8- isomers are dark red.

The authors are very grateful to Prof. A. I Kiprianov for his valuable counsel and advice during this work.

SUMMARY

1. By condensing o-nitroanisole with n-anisidine in the presence of pulverized potassium hydroxide, a mixture of 1,6- and 1,8-dimethoxyphenazines was obtained.

2. A similar reaction between o-nitrophenetole and m-phenetidine gave a mixture of 1,6- and 1,8-diethoxyphenazines.

3. These mixtures were separated by fractional crystallization from ligroin, alcohol and acetic anhydride.

4. The condensation of 3-methoxy-o-benzoquinone with 3-methoxy-o-phenylenediamine gave a mixture of 1,5- and 1,8-dimethoxyphenazines. These substances were separated with picric acid, since the 1,5- isomer does not form a picrate in alcoholic solution.

5. The structure of two new dialkoxyphenazines has been established.

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ULTRAVIOLET ABSORPTION SPECTRA OF BENZOTHIAZOLE DERIVATIVES

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The absorption spectra of benzothiazole derivatives have been examined on many occasions, partly in connection with the color of thiocyanine dyestuffs. Kiprianov and Petrunkin investigated the absorption by 2-methylbenzothiazole methiodide [1]. Lutsky and Sidorov determined the absorption curves for benzothiazole, 2-methylbenzothiazole, their ethiodides and certain other derivatives [2]. Boggust and Cocker [3], in a recent paper, present the absorption curves for benzothiazole in alcoholic solution, without referring to the work of Lutsky and Sidorov.

We investigated the absorption spectra in alcoholic solution, of certain benzothiazole bases, their quaternary salts, and the corresponding methylene bases, formed from the quaternary salts by the action of alkalies. Utilizing the data we obtained, we followed, by means of the ultraviolet absorption spectrum, the formation of a salt from 2-methyl-6-dimethylaminobenzothiazole by the action of alcoholic sulfuric acid solutions of different concentrations on this diacid base. The results we obtained are given later on.

We determined the absorption curves in alcoholic solution of the following 7 bases: 2-methylbenzothiazole, 2-ethyl-α-naphthothiazole, 2-methyl-5-dimethylamino- and 2-methyl-6-dimethylaminobenzothiazoles, 2-methyl-5-amino-, 2-methyl-6-amino-, and 2-methyl-7-aminobenzothiazoles.

The absorption spectra for the first five of these bases are presented in Fig. 1.

2-Methylbenzothiazole and 2-ethyl-α-naphthothiazole (Fig. 1, I and II) respectively, have a longer wave absorption band with fine structure: it consists of two narrow consecutive bands. Both bases also have a short wave. band of high intensity. The introduction of the amine groups into the benzene nucleus displaces the absorption band towards the long wave side and suppresses its fine structure (Fig. 1, III and IV). The amino substituted derivatives have one wide band, but in the short wave region there is only a deflection of the absorption curve without any pronounced maximum. The two dimethylamino-derivatives, 2-methyl-5-dimethylamino-benzothiazole and 2-methyl-5-dimethylbenzothiazole, give absorption bands in the considerably longer wave region, and the bands have a lower intensity (Fig. 1, V) than 2-methyl-6-dimethyl-aminobenzothiazole.(Fig. 1, IV). That this is not a chance phenomenon, is evident from Fig. 2.

The absorption curves for the 5-amino derivative (Fig. 2, I) and the 7-amino derivative (Fig. 2, III), are similar both in their region of absorption and the intensity of the bands, while the absorption band of the 6-amino-derivative is displaced to the shorter wave part of the spectrum, and has a very much larger intensity. (Fig. 2,II).

It should be noted that, among the isomeric aminoquinolines, containing amino groups on the benzene nucleus, no differences between the absorption curves of the 5- and 6- aminoquinolines have been reported [4].

In Fig. 3 we show absorption curves for five quaternary salts: the methiodide, ethiodide and benziodide of 2-methylbenzothiazole, 2-methyl-α-naphthothiazole ethiodide and 2-methyl-6-dimethylaminobenzothiazole methiodide.

The absorption bands for the first three salts are similar among themselves. They have one maximum in the 2700-2800 Å region and a bending of the curve in the low intensity absorption region.

The absorption bands of the quaternary salts of 2-methyl-α-naphthothiazole (Fig. 3, IV) and, in particular, of 2-methyl-6-dimethylaminobenzothiazole (Fig. 3, V) are displaced considerably towards the longer waves, and the absorption band of the latter compound is in the visible. Both compounds have also one very intense band in the short wave region.

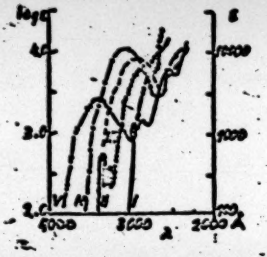


Fig. 1

I-2-Methylbenzothiazole; II-2-ethyl-α-naphthothiazole; III-2-methyl-6-aminobenzothiazole; IV-2-methyl-6-dimethylaminobenzothiazole; V-2-methyl-5-dimethylaminobenzothiazole.

Fig. 2

I-2-Methyl-5-aminobenzothiazole, II-2-methyl-6-aminobenzothiazole, III-2-methyl-7-aminobenzothiazole.

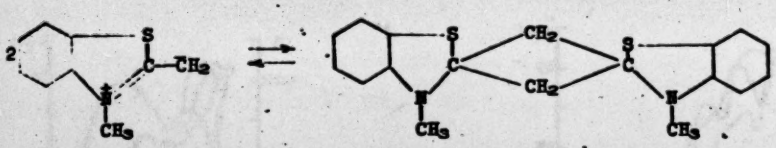
In Fig. 4 are given the absorption curves for two quaternary methiodides: 2-methylbenzothiazole (I), and 2-methyl-6-dimethylaminobenzothiazole (II), treated in alcoholic solution with three molecules of sodium ethylate.

Quaternary salts containing methyl groups in the 2-position are converted to methylene bases by the action of alkalies:

Fig. 4 includes the absorption curves for 2-methylbenzothiazole methiodide (III). Attention is focussed upon the similarity of this curve with the absorption curve for the corresponding methylene base which is located in the longer wave portion of the spectrum, (Fig. 4, I). Mumm [5], and later Kiprianov and Babichev [6], showed that methylene bases of the benzothiazole series exist in the form of dimers in equilibrium with the monomer:[1])

Judging by the absorption curve (Fig. 4, I), the equilibrium in dilute alcoholic solution is strongly displaced towards the monomer in the presence of excess alkali, so that only the monomer (in its polarized form) enters into the electronic structure of the quaternary salt. The dimer, being a more saturated derivative of the benzothiazole series, ought to absorb in the shorter wave region of the spectrum.

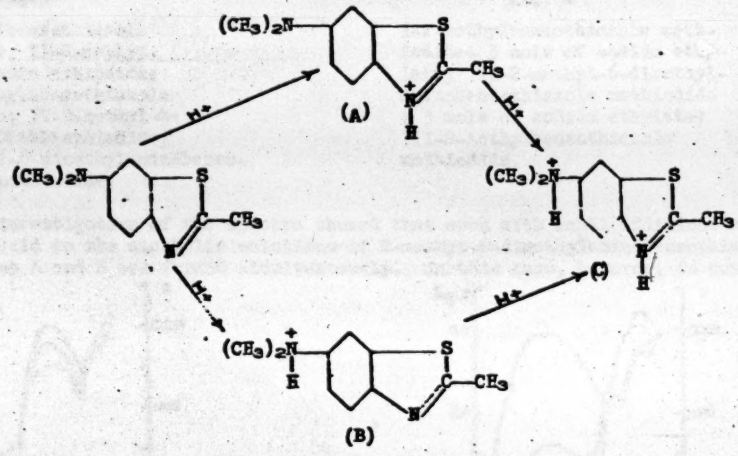
[1]) See following page.



Figs. 5,6, and 7 show the spectra for the diacid base 2-methyl-6-dimethylaminobenzothiazole, in alcoholic solution, in the presence of different quantities of sulfuric acid.

By following the absorption curves the formation of the salt of this base can be followed.

2-Methyl-6-dimethylaminobenzothiazole is converted by acids, which donate protons, into two different, singly charged cations A and B, and one doubly charged cation C:



It is known from the work of Steck and Ewing [4], relating to aminopyridines and aminoquinolines, that proton addition to these bases takes place in the first instance on the cyclic nitrogen atom. Actually, the absorption band for aminopyridines and aminoquinolines in acidified alcoholic solution is displaced towards the longer wave part of the spectrum. As is known, such a bathochromic effect is produced by the formation of quaternary salts. If proton addition does not take place on the nitrogen atom of the pyridine ring, but on the amino-group, it is bound by the electron pair of the nitrogen atom of the amino group; thereby eliminating the influence of this group on the spectrum. In this case the absorption curves are displaced to the short wave region.

Benzothiazole is a much weaker base than pyridine or quinoline, so that it is impossible to predict beforehand how far the cations A or B would be formed under the influence of the acid, in the first instance.

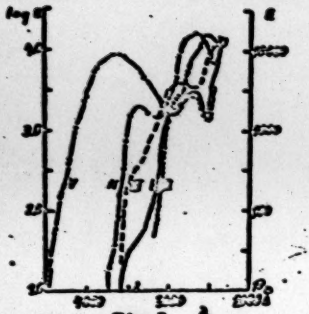


Fig.3

I-2-methylbenzothiazole methiodide; II-2-methylbenzothiazole ethiodide; III-2-methylbenzothiazole benziodide; IV-2-methyl-α-naphthothiazole ethiodide; V-2-methyl-6-dimethylaminobenzothiazole methiodide.

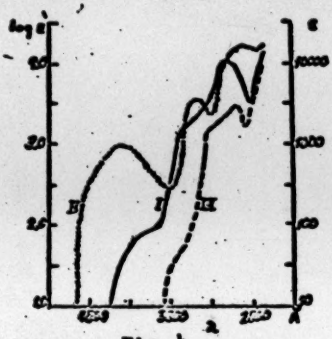


Fig. 4

I-2-methylbenzothiazole methiodide+ 3 mols of sodium ethylate; II-2-methyl-6-dimethylaminobenzcthiazole methiodide + 3 mols of sodium ethylate; III-2-methylbenzothiazole methiodide.

The investigation of the spectra showed that even with small additions of sulfuric acid to the alcoholic solutions of 2-methyl-6-dimethylaminobenzothiazole, the cations A and B are formed simultaneously. In this case, however, in contrast

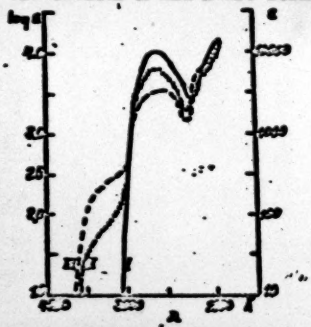


Fig. 5

I-2-methyl-6-dimethylaminobenzothiazole; II-2-methyl-6-dimethylaminobenzothiazole + 1 mol of sulfuric acid; III-2-methyl-6-dimethylaminobenzothiazole + 5 mol of sulfuric acid.

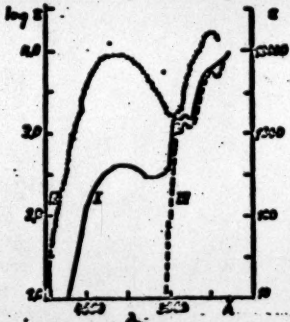


Fig. 6

I-2-methyl-6-dimethylaminobenzothiazole + 100 mol sulfuric acid; II-2-methyl-6-dimethylaminobenzothiazole methiodide; III-2-methylbenzothiazole.

to what occurs with amino pyridines and aminoquinolines, salt formation occurs,

preferentially at the amino group.

Curve 1 of Fig. 5 shows the absorption spectrum of the base in neutral alcoholic solution. When 1 mole of sulfuric acid is added, two changes in the absorption curve (Fig. 5, II) are to be noted. A new band appears in the low intensity region at 3500-4000 Å, and the principal absorption band at 3050 Å is lowered in intensity.

It seems reasonable to suggest that the appearance of the new band, with a low intensity, is caused by the emergence of the cation A in solution. As a matter of fact, the absorption spectrum for cation A ought to be similar to the absorption spectrum for the cation of the quaternary salt:

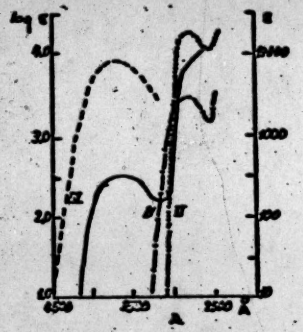
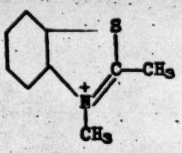


Fig. 7

I-2-methyl-6-dimethylaminobenzothiazole + 1000 mol. of H_2SO_4; II-2-methyl-6-dimethylaminobenzothiazole + 10,000 mol of H_2SO_4; III-2-methyl-6-dimethylbenzothiazolemethiodide; IV-2-methylbenzothiazole ethiodide.



which gives a wide band with a maximum at 3660 Å (Fig. 3, V). Precisely such a band, with a maximum at 3600 Å develops from the inflection on the Curve II, Fig. 5, when the concentration of the sulfuric acid is increased.

Without a knowledge of the molar extinction coefficient of the cation A, it is difficult to make any estimate of the concentration of this cation in the solution, from Curves I and II in Fig. V, or from Curve I of Fig. 6 and Curve I of Fig. 7.

Undoubtedly the concentration of cation A is small here. If it be assumed that the molar extinction coefficient of cation A is of the same magnitude as that of the corresponding quaternary salt (ε = 9000, Fig. 3, V) then the quantity of base which is converted to the cation A form by the addition of 1 mol of H_2SO_4 (Fig. 5, II) is 1% and, on addition of 5 mol of acid it is about 2% (Fig. 5, III), while in the presence of 100 mol of acid it becomes about 4%.

The quantity of the cation B may be assessed from the lowering of the maximum absorption at 3060 Å. The absorption curve for cation B ought to be similar to that for 2-methyl-benzothiazole, which does not absorb at 3060 Å (Fig. 1, I). If we assume that the lowered intensity of the maximum at 3060 Å is proportional to the quantity of cation B that is formed, then addition of 1 mol of H_2SO_4 (Fig. 5, II) causes 60-70% of the base to go over into the ion B, and 5 mol acid causes a 70-80% change.

Curve I of Fig. 6 is unusual. This curve corresponds to the absorption by a solution of 2-methyl-6-dimethylaminobenzothiazole, to which 100 mol of sulfuric acid have been added. Here the band corresponding to cation A,

(in large concentration (max. at about 3600 Å), is very clearly in evidence, the band at 3060 Å) is absent, and in its place there is a band with fine structure (two maxima at 2800 and 2900 Å) strongly resembling those which appear on the absorption curve of 2-methylbenzothiazole. This band undoubtedly corresponds to ion B.

Apparently, on addition of 100 mol. of sulfuric acid per mol. of base the whole of the latter is converted to the singly charged ions, of which only a small proportion are of A, and the vast majority are of B.

Curves I and II of Fig. 7 indicate what happens when the concentration of sulfuric acid is increased further. When 1000 mol. of acid are added to 1 mol. of base, the doubly charged ion C is formed. It is formed mainly at the expense of ion B, which no longer appears on Curve I of Fig. 7 (absence of fine structure on the curve) while at the same time the concentration of ion A is only slightly lowered. Finally, with 10,000 mol. of acid per mol. of base (Fig. 7, II), the base is completely converted to the doubly charged ion C, a state of affairs which is revealed by the fact that the curve has practically the same form as that for the quaternary salt of 2-methylbenzothiazole (Fig. 7, IV).

We observed quite similar phenomena - salt formation on the N of the thiazole ring difficult, and easy on the N of the amine - in the action of sulfuric acid on other amino derivatives of benzothiazole: 2-methyl-6-amino-, 2-methyl-7-amino-, and 2-methyl-5-dimethylaminobenzothiazoles. The curves for these cases are not presented here.

The formation of the diacid salt of 2-methyl-6-dimethylaminobenzothiazole proceeds with difficulty and, as we have seen, is only complete when 10,000 mol. of acid per mol. of base have been added. We observed the same phenomenon in the action of sulfuric acid upon alcoholic solutions of 2-methyl-5-dimethylaminobenzothiazole methiodide.

With 100 mol. of sulfuric acid per mol. of quaternary salt, the intensity of the absorption band at 3660 A, due to this salt, had hardly been lowered at all. A sharp fall in the intensity of absorption in this region was observed only when 1000 mol. of acid per mol. of salt were present.

The photographic method which we used for determining the absorption curves was not sufficiently accurate to permit reliable quantitative calculations. But we used it to establish beyond doubt that, in contrast to aminoquinolines, the more basic centers in the molecules of the aminobenzothiazoles are the amino groups, and the less basic ones are the N atoms in the thiazole rings.

EXPERIMENTAL

The photographing of the absorption spectra was made on a Hilger medium quartz spectrograph (model E-298), using a double rotating sector photometer. The spectrographs obtained were examined visually, with subsequent correction of the positions of the maxima with a microphotometer. We used quartz cuvettes having layer thicknesses of 100, 50, 10, and 1mm (± 0.005mm). The source of light was a condensed spark between tungsten electrodes. In those cases where the alcoholic solution was diluted with acid or alkali, the photography was made on different layer thicknesses, without changing the concentration of the solution under investigation.

The ethyl alcohol was purified by standing it for 24 hours in contact with iodine, and then distilling it 3-4 times, until the alcohol in a layer 10mm was optically clear to 2150 A. The sodium ethylate was prepared immediately before making the photographs by dissolving the calculated weight of metallic sodium in

ethyl alcohol.

The data obtained in photographing the spectra, are given in the table.

Compounds Investigated

1. 2-Methylbenzothiazole was purified by repeated vacuum distillation. Colorless oil, boiling at 102°/3mm.

2. 2-Ethyl-α-napthothiazole was purified by vacuum distillation (162°/3mm). Colorless crystals, m.p.25° (Zubarovsky[7], 25°).

Results of photographing the spectra of alcoholic solutions of benzothiazole derivatives

Fig. No.	Curve No.	Derivative	Maximum λ(Å) 1	2	3	ε 1	2	3
1	I	2-methylbenzothiazole, 10^{-2}—10^{-4} M	2940	2830	2520	1300	1400	6000
1	II	2-ethyl-α-naphthothiazole, 10^{-3}—10^{-4} M	3330	3245	2855	500	350	6000
1	III	2-methyl-6-aminobenzothiazole, 10^{-2}—10^{-4} M	2895	--	--	800	--	--
1	IV	2-methyl-6-dimethylaminobenzothiazole, 10^{-2}—10^{-4} M . . .	3050	--	--	10000	--	--
1	V	2-methyl-5-dimethylaminobenzothiazole, 10^{-2}—10^{-4} M . .	3370	--	--	2000	--	--
2	I	2-methyl-5-aminobenzothiazole, 10^{-2}—10^{-4} M	3240	--	--	2600	--	--
2	II	2-methyl-6-aminobenzothiazole, 10^{-2}—10^{-4} M	2895	--	--	800	--	--
2	III	2-methyl-7-aminobenzothiazole, 10^{-2}—$5\cdot10^{-4}$ M	3150	2380	--	2600	16000	--
3	I	2-methylbenzothiazole methiodide, 10^{-2}—10^{-4} M	2695	--	--	3000	--	--
3	II	2-methylbenzothiazole ethiodide, 10^{-4}—10^{-4} M	2780	--	--	2800	--	--
3	III	2-methylbenzothiazole pheniodide, 10^{-2}—10^{-4} M	2840	--	--	4000	--	--
3	IV	2-methyl-α-naphthothiazole, ethiodide, 10^{-2}—10^{-4} M . . .	3350	2690	--	2000	16000	--
3	V	2-methyl-6-dimethylaminobenzothiazole methiodide, 10^{-2}—10^{-4} M	3360	2515	--	9000	16000	--
4	I	2-methylbenzothiazole methiodide, 10^{-3} M + 3 mol. Sodiumethylate.	2780	--	--	10000	--	--

Table continued on the following page.

Fig. No.	Curve No.	Derivative	Maximum λ(Å) 1	2	3	ε 1	2	3
4	II	2-methyl-6-dimethylaminobenzothiazole methiodide, 10^{-5}M + 3 mol sodium ethylate	4090	3150	2610	900	3500	16000
5	II	2-methyl-6-dimethylaminobenzothiazole, 10^{-5} M + 1 mol. H_2SO_4	3050	--	--	6000	--	--
5	III	Ditto + 5 mol. H_2SO_4	3010	--	--	3500	--	--
6	I	Ditto + 100 mol. H_2SO_4	3550	2990	2800	400	1600	1600
7	I	Ditto + 1000 mol. H_2SO_4	3600	--	--	300	--	--
7	II	Ditto + 10000 mol. H_2SO_4	2760	--	--	20000	--	--

3. 2-Methyl-6-dimethylaminobenzothiazole was purified by repeated crystallization from water after filtration through active charcoal. Colorless needles, m.p. 102° (Fries and Walter [8], 102°.

4. 2-Methyl-6-amino benzothiazole was obtained by reduction of 2-methyl-6-nitrobenzothiazole with tin and HCl. Colorless needles (from water), m.p. 126° (Kiprianov and Sich, [9], 124°.)

5. 2-Methyl-7-aminobenzothiazole was purified by repeated recrystallization from water. Colorless flat needles, m.p. 96.5° (Sich [10], 96.5°.)

6. 2-Methyl-5-dimethylaminobenzothiazole was purified by recrystallization from water. Colorless tablets, m.p. 86° ([11], 85-86°.)

7. 2-Methyl-6-dimethylaminobenzothiazole was purified by recrystallization from aqueous alcohol, colorless needles, m.p. 74° (Kiprianov and Sich [9], 74°.)

8. 2-Methylbenzothiazole methiodide was purified by repeated crystallization from aqueous alcohol. Colorless prisms, m.p. 222°.

9. 2-Methylbenzothiazole ethiodide was purified by repeated crystallization from aqueous alcohol and carbon. Colorless prisms, m.p. 198° (Mills [12], 190-192°)

10. 2-Methylbenzothiazole benziodide was purified by repeated crystallization from water. Colorless needles, m.p. 232° (Zubarovsky [7], 232°.)

11. 2-Methyl-α-naphthothiazole ethiodide was purified by repeated crystallization from water. Colorless prisms, m.p. 234° (Kiprianov and Ushenko [13], 234°.)

12. 2-Methyl-6-dimethylaminobenzothiazole methiodide was purified by repeated crystallization from aqueous alcohol and carbon. Pale yellow platelets, m.p. 258° (Kiprianov and Sich [9] 250°.)

Compounds 3, 5, 6, 7 and 12 were synthesized by E. A. Sich, 2 and 11 by V. M. Zabarovsky, and 10 by I. K. Ushenko, to all of whom we express our thanks.

SUMMARY

1. The absorption spectra of alcoholic solutions of 2-methylbenzothiazole and its derivatives, containing amino groups on the benzene ring, of 2-methyl-α-naphthothiazole, and of a series of quaternary salts of the benzothiazole derivatives, have been investigated.

2. The absorption curves of two methylene bases, formed by the action of sodium ethylate on alcoholic solutions of 2-methyl-benzothiazole and 2-methyl-6-

dimethylaminobenzothiazole methiodides have been determined.

3. The absorption curves of amino and dimethylamino derivatives of 2-methylbenzothiazole in alcoholic solution, in the presence of sulfuric acid, were examined. The absorption by 2-methyl-6-dimethylaminobenzothiazole was investigated with different concentrations of sulfuric acid in the solution.

4. From the absorption curves for 2-methyl-6-dimethylaminobenzothiazole in alcoholic solution, at increasing concentrations of sulfuric acid, it was concluded that the formation of a salt of this base proceeds more easily on the amino group, than on the heterocyclic N atom.

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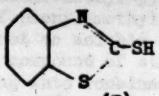
INVESTIGATIONS IN THE FIELD OF BENZOTHIAZOLE DERIVATIVES

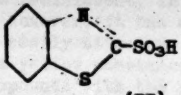
PREPARATION OF 1-BENZOTHIAZOLYL-3-METHYL-5-PYRAZOLONE

L. S. Efros and L. R. Davidenkov

In recent years it has been reported in the literature that by oxidizing 2-mercaptobenzothiazole (I), the corresponding sulfo acid may easily be obtained (II), the sulfo group of which can, under very mild conditions, be replaced by hydroxyl, the amino group, hydrazine residues and other nucleophilic radicals.



(I)



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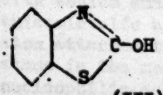
This simple method of obtaining a range of benzothiazole derivatives appeared to us to be of great interest, and consequently we decided to investigate the possibility of utilizing it.

According to patent claims [1] the sulfo acid (II) is formed by oxidizing 2-mercaptobenzothiazole (I) with alkaline solution of sodium hypochlorite or with hydrogen peroxide. However, the use of these oxidants was not successful, and only by using alkaline permanganate were we able to obtain, smoothly and in good yield, the 2-sulfo acid of benzothiazole in the form of the potassium salt.

By the action of hydrochloric acid on the concentrated aqueous solution of the potassium salt of the sulfo acid, the free acid was liberated in the form of small needles, dissolving easily in water and in ethyl alcohol. However, even after very gentle heating, the 2-sulfo acid was hydrolyzed, 2-hydroxybenzothiazole (III) [2] and sulfuric acid being formed.

By heating the potassium salt of 2-benzothiazolesulfo acid with an aqueous solution of hydroxylamine we obtained, in good yield, the compound 2-benzothiazole-hydroxylamine (IV) not previously described. The structure of this very easily oxidized substance was confirmed by reducing it to 2-aminobenzothiazole (V).



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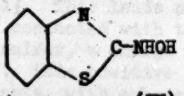

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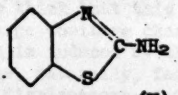
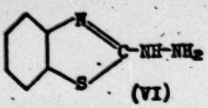


(V)

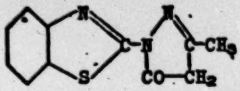
The latter we obtained by the method given in the literature, and by another route - heating the potassium salt of the sulfo acid (II) with aqueous ammonia at 125° [3].

Finally, by heating the potassium salt of the sulfo acid with hydrazine in aqueous solution, we obtained 2-benzothiazolyl-hydrazine (VI) [4]. From this product it appeared of interest to obtain the benzothiazole analog of 1-phenyl-3-methyl-5-pyrazolone (VII), of importance in the manufacture of medicinals and dyes. We discovered very general directions for such a synthesis in a patent [4].

Actually, after a series of failures, we obtained from the reaction of benzothiazolyl-hydrazine (VI) with ethylacetoacetate, a very crude product in 50% of the theoretical yield, which, after many purifications, was shown to be the



(VI)

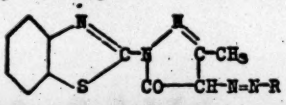


(VII)

pyrazolone derivative (VII), whose structure was confirmed by analysis, and by its properties. The large amount of impurity, and the low yield, induced us to try to obtain it another way, by using instead of acetoacetic ester, acetoacetic acid amide. (The latter can easily be prepared by carefully dissolving diketene in aqueous ammonia). In this way it was shown that the reaction between benzothiazolyl-hydrazine (VI) and acetoacetic amide gives a nearly quantitative yield of the quite pure pyrazolone derivative (VII), thus making the latter quite an accessible product.

Benzothiazole-methyl-pyrazolone (VII) is reminiscent, in many of its chemical properties, of phenyl-methyl-pyrazolone but, however, it has a smaller basicity and is therefore not so soluble in acids. It is easily nitrated, forming the corresponding nitro compound of structure (VIII), a yellow substance, soluble in alkalies, easily entering into combination with azo compounds with the formation of orange yellow azo-dyes. These have the general formula (IX), the simplest of which, obtained by diazotizing aniline, we analyzed.

(VIII)



(IX)

Benzothiazole-methyl-pyrazolone has an affinity for cotton fibers, which makes it possible to use it as an azo dye.

Thus our experiments completely confirmed what is unusual in sulfo acids, namely, the ease with which the sulfo acid group of 2-benzothiazole sulfo acid (II) is displaced by nucleophilic substituents. This peculiarity stands out particularly sharply in hydroxyl substitution. The majority of sulfo acids, as is well known, undergo this reaction only under the rather severe conditions of alkaline fusion, while 2-benzothiazolesulfo acid is converted to the hydroxy compound after a short period of heating in aqueous solution.

In contrast with this desulfonation, which proceeds with most sulfo acids fairly smoothly, can only be brought about for the 2-benzothiazole sulfo acid by treatment with sodium amalgam [1]. This leads one to think that this property of the 2-benzothiazolesulfo acid is connected with the large positive charge carried by the carbon atom attached to the sulfur, a charge which is induced by the nitrogen and sulfur atoms in the molecule. This positive charge, naturally, facilitates the entry of nucleophilic substituents, with subsequent displacement of the sulfo group.

EXPERIMENTAL

2-Benzothiazolesulfo acid. 20 g of technical mercaptobenzothiazole ("kaptaks") was dissolved at room temperature in a solution of 9 g KOH in 75-80 ml of water. Then, with uninterrupted stirring, 400 ml of 10% potassium permanganate was added to this in a fine stream during about 20 minutes, the solution being at 60-70°. The reaction proceeded with liberation of heat, but special cooling was not required. The end of the oxidation was indicated by the appearance of excess permanganate in the solution. The mixture was stirred for a certain time longer, during which the excess of permanganate usually disappeared (in cases where this did not happen a small quantity of hydrosulfite was added). After this the solution, containing the sulfo acid, was separated from the precipitated MnO_2, neutralized with acetic acid;

(a small excess of this did no harm) and evaporated until crystallization commenced. On cooling, the crystals which separated settled out well. The yield was 50-60% of the theoretical. For a final purification the product may be recrystallized from water, using active carbon. 2-Hydroxy-benzothiazole may very easily be obtained from the product. For this purpose a solution of the potassium salt of the acid was acidified with hydrochloric acid to a final acid reaction, and boiled for some time, until the mixture had no odor of sulfur dioxide. 2-Hydroxybenzothiazole separated in the form of an oil, which solidified on cooling. The product can be recrystallized from dilute ethyl alcohol (1/3). Its properties agree with those quoted in the literature [5].

2-Benzothiazolyl-hydroxylamine. 10 g of hydroxylamine hydrochloride was dissolved in 50 ml of hot 20% solution of potassium 2-benzothiazole-sulfonate, heated to boiling and 6 g of soda ash was carefully added. After three minutes the reaction had practically finished, and the reacting mixture was rapidly cooled, filtered, and washed with water. About 6 g of a white product was obtained, which is 80% of the theoretical.

2-Benzothiazole-hydroxylamine crystallizes from aqueous alcohol in the form of small needles; however in the course of this crystallization it becomes considerably oxidized. The compound dissolves easily in dilute mineral acids, while in alkalies and ammonia it is very rapidly decomposed, giving a bright raspberry color. When heated in a capillary tube it chars, but does not melt. Its solution in mineral acid instantaneously decolorizes permanganate solution, forming an orange colored substance.

0.0976 g substance: 13.7 ml N_2 (14°, 758 mm). Found %: N 16.65. $C_7H_6ON_2S$. Calculated %: N 16.87.

Titration with permanganate gave the following results: 0.1563 g substance: 7.5 ml (T = 0.00196 g O_2); 0.1327 g substance: 6.9 ml (T = 0.00196 g O_2); 0.0994 g substance: 5.0 ml (T = 0.00196 g O_2). Equivalent weight found: 85.0, 78.4, 81.1. $(C_7H_4NS)NHOH$. Calculated equivalent weight: 83.

Reduction of 2-benzothiazole-hydroxylamine to aminobenzothiazole. To a 3-4% solution of the compound in dilute hydrochloric acid, heated to 60-70°, a small quantity of zinc dust was added. Reduction was carried on until such time as a sample withdrawn from the mixture failed to give a raspberry color when made alkaline. The solution was then cooled, filtered from suspended zinc, and rendered strongly alkaline. The product was extracted with ether. The ethereal extract was evaporated to dryness, when 2-aminobenzothiazole crystallized in the form of leaflets. Recrystallized from benzene, it had an m.p. of 126°, which temperature was not depressed by mixing the substance with 2-aminobenzothiazole, obtained in completely quantitative yield by heating potassium benzothiazolesulfonate with aqueous ammonia in a sealed tube at 125°.

2-Benzothiazole-hydrazine. 10 g of potassium benzothiazole sulfonate was dissolved in 80 ml of hot water and 5 ml of hydrazine hydrate were added. The solution, contained in a flask provided with a reflux condenser, was stirred for 30 minutes over boiling water. Before long the mixture set solid with the crystallization of the benzothiazole-hydrazine. The reaction product was filtered off and washed with cold water. For a further purification it was dissolved in dilute hydrochloric acid, filtered from a small amount of dark-colored impurity, precipitated with ammonia and crystallized from ethyl alcohol. The yield was 6 g, nearly 90% of the theoretical. Colorless needles (from alcohol), melting at 194-195° (in a patent [4],205° is mentioned, and elsewhere [6], 195°.)

Heated with benzaldehyde in alcoholic solution it gives the corresponding hydrazone of benzaldehyde, which does not dissolve in alcohol, which, after puri-

fication, melts at 220° (reported as 221-222° [6]).

1-(2'-Benzothiazole)-3-methyl-5-pyrazolone. (a) Synthesis with acetoacetic ester. 4 g of 2-Benzothiazolyl-hydrazine, as a saturated solution in boiling alcohol, was mixed with 3.7 ml of acetoacetic ester and boiled for 4 hours under a reflux condenser. After cooling (occasionally stirring with a glass rod), the product crystallized. It was washed on the filter funnel with a small quantity of ethyl alcohol and dried. About 3 g of a brown product (about 50% of the theoretical) was obtained, which was finally purified by a single recrystallization from alcohol.

(b) Synthesis by using diketene. To 10 ml of a solution of ammonia, cooled on ice, 2.5 ml of diketene was added slowly with vigorous shaking. After the latter had completely dissolved, the solution was acidified with hydrochloric acid until it gave a clear (acid) reaction to Congo red, and then 4 g of benzothiazolyl-hydrazine in 80 ml of 3-5% hydrochloric acid was mixed in. The mixture was heated for 15 minutes on a boiling water bath. At the end of this time, the mass set solid from the crystallization of the benzothiazolyl-methyl-pyrazolone which had been formed. 5.6 g, nearly the theoretical yield, was obtained, which after filtering off, washing with water, and drying, was nearly pure. After one recrystallization from alcohol it was found to be chemically pure and melted at 225°. The product was identical with that obtained by the previous method.

Benzothiazolyl-methyl-pyrazolone dissolves easily in dilute alkalies, but is almost insoluble in dilute acids and cold alcohol. The alcoholic solution gives a dark brownish-violet color with ferric chlorides.

0.1416 g substance: 22.3 ml N_2 (21°, 763mm); 0.1014 g substance: 15.9 ml N_2 (21°, 763 mm). Found %: N 18.36, 18.28. $C_{11}H_9ON_3S$. Calculated %: N 18.18.

4-Nitroso-1-benzothiazolyl-3-methyl-5-pyrazolone. To a solution of 1.2 g of benzothiazolyl-methyl-pyrazolone in conc.HCl, a solution of 0.4 g of sodium nitrite was added, dropwise. The nitroso product, which is insoluble in acids, commenced to separate almost immediately. After one hour it was filtered off, washed with water and dried. The yield was 1.2 g.

Nitroso-benzothiazolyl-methyl-pyrazolone crystallizes from acetic acid as a bright yellow product, soluble in dilute alkalies, with a certain deepening of its color. M.p. 254-255°.

0.0912 g substance: 17.0 ml N_2 (21°, 757 mm); 0.0915 g substance: 17.2 ml N_2 (21.5°, 757 mm). Found %: N 21.56, 21.70. $C_{11}H_8O_2N_4S$. Calculated %: N 21.54.

Azo compound from 1-benzothiazolyl-3-methyl-5-pyrazolone. To a saturated solution of the pyrazolone derivative in 3% alkali, cooled with ice, a solution of diazotized aniline was slowly added, or else a solution of diazotized sulfanilic acid, until an excess of azo compound remained, as shown by the reaction with H-acid in the supernatant liquid. After some hours the product was filtered off and washed with water. The azo dye obtained with diazotized sulfanilic acid is, in the form of its sodium salt, a yellow-orange substance, soluble in water, dyeing wool a good fast yellow. The dye obtained with diazotized aniline crystallizes well from acetic acid, in orange needles, which were analyzed. M.p. 237-238°.

0.1320 g substance: 24.0 ml N_2 (21°, 756 mm); 0.0763 g substance: 13.6 ml N_2 (21°, 759 mm). Found %: N 20.67, 21.00. $C_{17}H_{13}ON_5S$. Calculated %: N 20.9.

SUMMARY

1. In confirmation of patent claims, 2-benzothiazolesulfonic acid was obtained by the oxidation of 2-mercaptobenzothiazole, in an alkaline environment. The sulfo group was easily replaced by hydroxyl and amine groups, and by hydroxylamine and hydrazine residues.

2. From 2-benzothiazolyl-hydrazine, by condensation with acetoacetic ester, or with acetoacetic acid amide, 1-benzothiazolyl-3-methyl-5-pyrazolone was obtained, the yield in the second case approaching the theoretical. The nitroso and azo derivatives of this pyrazolone compound were obtained.

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[2] DRP, 615131; Frdl., 22, 324.

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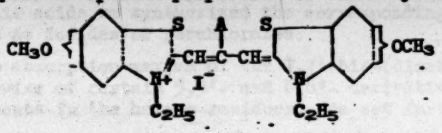
INVESTIGATIONS IN THE FIELD OF CYANINE DYES

VI. PROPERTIES OF 7,7-BIS-(DIMETHYLAMINO)-THIACARBOCYANINES

I. I. Levkoev and B. S. Portnaya

It was shown earlier [1] that the position of the methoxy group in the hetero-residues of symmetrical dimethoxythiacarbocyanines (I) exerts a strong influence upon the optical properties of these dyestuffs:



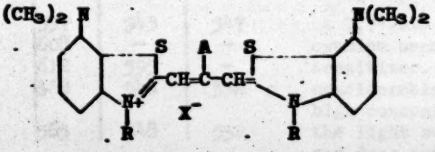
(I)

It has been reported that the maximum absorption of the 5,5'- and 6,6'-dimethoxythiacarbocyanines is displaced considerably towards the longer wave part of the spectrum, in comparison with that of the 4,4'- and 7,7'- derivatives. Kiprianov and Dashevskaya [2,3] likewise found that the maximum absorption of 5,5'- and 6,6'- dihydroxythiacarbocyanines lies in a longer wave part of the spectrum than does that of the 4,4'- and 7,7'- derivatives.

It appeared interesting to examine whether this correlation was maintained on introduction, into the heterocyclic residue of the thiacarbocyanine, of strongly electron-donating substituents such as the dimethylamino group, which usually deepens the color.

The 5,5'- and 6,6'-bis-(dimethylamino)-thiacarbocyanine dyestuffs, described in certain patents, have been studied in detail by Kiprianov and Sich [5,6]. This study has shown that the introduction of the dimethylamino group into the 5,5'- and 6,6'- positions causes nearly equal bathochromic displacements of the absorption maxima (51 mμ and 55 mμ).

We synthesized and studied the 7,7'-bis-(dimethylamino)-thiacarbocyanine dyestuff (II). The synthesis commenced from the disubstituted thiacyanine dye, with the dimethylamino groups in the ortho position to the hetero-atom of the benzothiazole nucleus, a compound not previously described in the literature.



(II)

To obtain the initial base, 7-dimethylamino-2-methylbenzothiazole, we investigated the interaction of m-thioacetamino-dimethylaniline with potassium ferricyanide [7]. As was shown earlier [8] when thioacetyl-m-anisidine is oxidized, closure of the thiazole ring occurs both in the ortho and the para position to the methoxy group. Hence it may be expected that, in this reaction, m-thioacetylaminodimethylaniline will give rise to a mixture of 7- and 5-dimethylamino-2-methylbenzothiazole. However, upon interaction of m-thioacetylaminodimethylaniline with potassium ferrocyanide in alkaline solution, only one base was obtained melting at 43-44°, (5-dimethylamino-2-methylbenzothiazole has an m.p. of 83-84°), the picrate of which had its melting point lowered when mixed with the picrate of 5-dimethylamino-2-methylbenzothiazole.

Thus, oxidation of p-thioacetaminodimethylaniline induces closure of the thiazole ring in the ortho position to the dimethylamino group, so that only 7-dimethylamino-2-methylbenzothiazole is formed.

By condensing the methiodide or the methyl and ethyl-p-toluenesulfonates of 7-dimethylamino-2-methylbenzothiazole with the ethyl esters of ortho carboxylic acids we synthesized the corresponding carbocyanines, which were isolated as iodides or perchlorates.

The absorption maxima of the 7,7'-bis-(dimethylamino)-thiacarbocyanines and likewise of certain 5,5'- and 6,6'- derivatives, and of dyes with no substituents in the hetero-residues, are set forth in Table 1.

From the table it can be seen that the entry of two dimethylamino groups into the thiacarbocyanine molecule, in the 7,7'- position, causes a considerably smaller bathochromic displacement of the absorption maximum than does the entry of this group into the 5,5'- and 6,6' positions. (For ethylates of dyes, not substituted in the chain, the figures are 11, 51, and 55 mμ. Thus, the great difference between the effects of electron-donating substitutents in the 5,5'-positions on the one hand, and in the 7,7'-positions on the other, on the color of thiacarbocyanine dyestuffs, is conserved also in cases where the substituents are more electropositive. This result, briefly published by one of us earlier [10], is in agreement with data obtained recently by Sich [11], relative to the color of isomeric diaminothiacarbocyanines. The increase in the color of the 4,4'- and 7,7'-disubstituted thiacarbocyanines is evidently connected with the fact that in these dyes, there is less abstraction of electrons from the polymethine chain, than in those which are substituted in the 5,5'- and 7,7'- positions.

Table 1

Position of the $N(CH_3)_2$ group	Absorption Max. (in mμ) Substituent in the 9-position		
	H	CH_3	C_2H_5
Ethylates			
–	557	543	547
5,5' . . .	608	–	–
6,6' . . .	612	595	–
7,7' . . .	568	548	552
Methylates			
7,7' . . .	565	548	552

The absorption maxima of alcoholic solutions of 7,7'-bis-dimethylamino-thiacarbocyanines, as in the cases of the 5,5'- and 6,6'- derivatives, [10,12,13], is displaced towards the shorter wave region by acidification (cf. [11]).

7,7'-bis-(dimethylamino)-thiacarbocyanine seems to be a rather weak sensitizer. It does not exhibit any considerable fogging action, and in high concentration markedly reduces the light sensitivity of emulsions, and does not induce second order sensitization.

EXPERIMENTAL

m-Nitrodimethylaniline. This was obtained by Groll's method [14], involving the nitration of dimethylaniline in the presence of excess sulfuric acid. To a solution of 60.5 g of dimethylaniline in 1210 g of sulfuric acid (d. 1.84), a mixture of 58 g of nitric acid (d. 1.36) and 182 g of sulfuric acid (d. 1.84) was added. This admixture was made gradually at 0-3°, with stirring. After 4-5 hours, the reaction mixture was poured into 3 liters of water, the m-nitrodimethylaniline which separated was filtered off, the filtrate carefully

neutralized with aqueous ammonia until the crystals of the dye commenced to separate. The liquid was rapidly filtered, and the liquid neutralized with aqueous ammonia. m-Nitrodimethylaniline was filtered off, washed with water and afterwards dried (weight 46.16 g). It was then crystallized from ethyl alcohol. The yield was 42.8 g (51.5% of theory). Red prisms melting at 60° (Groll quotes 60-61°). The yield of p-nitrodimethylaniline was 28 g (33.7% of theory).

m-Aminodimethylaniline. 24.9 g of m-nitrodimethylaniline was slowly introduced into a cooled solution of 132 g of stannous chloride in 130 ml of hydrochloric acid (d. 1.19). The reaction mass was then heated on a water bath for 30 minutes, cooled, shaken vigorously with a 30% solution of caustic soda, and the amine extracted with ether. The extract was dried with potash, the ether distilled off, and the residue distilled in vacuum. At 36 mm all the product distilled over at 158°. The yield of 19.6 g was 96% of theory. Colorless oil, rapidly darkening in air. By reducing m-nitrodimethylaniline (24.9 g) at 0-2° with zinc dust (55 g) and hydrochloric acid (d. 1.1) (260 ml), with analogous further treatment, the amine was obtained in 80% of the theoretical yield.

m-Acetoaminodimethylaniline. To 20.4 g of m-aminodimethylaniline 19.9 g of acetic anhydride was added gradually. On the following day, the crystalline deposit which had appeared was filtered off and washed with water. 16.1 g, melting at 87° [15]. A further 8.4 g was separated from the filtrate, after dilution with water and neutralization with potash. This melted at 85°, the general yield was 24.5 g approximately 91.8% of theory). Colorless prisms (from alcohol).

Picrate - yellow prisms (from alcohol) M.p. 187°.

Found %: N 17.15. $C_{16}H_{17}O_8N_5$. Calculated %: N 17.20.

m-Thioacetoaminodimethylaniline. Into a boiling solution of 5 g of m-acetoaminodimethylaniline in 25 ml of dry xylene, 3.1 g of ground phosphorus pentasulfide was introduced with stirring, and the reaction mass was boiled for 1½ hours. The xylene solution was decanted, the residue washed with benzene at the boil, and the mixture of xylene and benzene extracted with 10% caustic potash (5 times with 20 ml). The alkaline solution was acidified with acetic acid, and m-thioacetoaminodimethylaniline was separated by passing CO_2 through the solution. The product was isolated in the form of a yellow oil, which was extracted with ether, and the extract was dried with potash. The residue, after distilling off the ether was a thick yellow oil, which could not be made to crystallize. The yield was 1.48 g (27.2% of theory). For analysis the substance was converted to its picrate (yield 90% of theory) which was purified by crystallization from alcohol. Yellow prisms, melting at 168°.

Found %: N 16.71. $C_{16}H_{17}O_7N_5S$. Calculated %: N 16.54.

7-Dimethylamino-2-methylbenzothiazole. A solution of 5 g of m-thioacetoaminodimethylaniline in 40 ml of 8% caustic potash was gradually added, with constant stirring, to a solution of 17 g of potassium ferricyanide in 85 ml of water, cooled to 0-1°. On the following day the reaction mixture was extracted with ether. The extract was dried with potash, and the residue, after distilling off the ether (4.6 g), was converted to the picrate. The yield of picrate was 8.2 g (75.5% of theory). M.p. 168°. The picrate was decomposed with soda, the separated base extracted with ether, the extract dried with potash, and the residue, after distilling off the ether, was itself distilled

Name of dyestuff	Quantity of 7-dimethylamino-2-methylbenzothiazole methiodide (g)	Quantity of methyl and ethyl-p-toluenesulfonates of 7-dimethylamino-2-methylbenzothiazole	Quantity and kind of ethyl orthocarboxylate	Quantity of pyridine (in ml)	Time of heating (in minutes)	Yield of dyestuff (% of theory)
3,3'-Dimethyl-7,7'-bis-(dimethylamino)-thiacarbocyanine iodide	0.33	-	OE-1 0.3	0.8	30	72.7
3,3',9-Trimethyl-7,7'-bis-(dimethylamino)-thiacarbocyanine perchlorate	-	0.38	OE-2 0.32	0.8	30	34
3,3'-Dimethyl-9-ethyl-7,7'-bis-(dimethylamino)-thiacarbocyanine perchlorate	-	1.13	OE-3 1.06	2	40	37.6
3,3'-Diethyl-7,7'-bis-(dimethylamino)-thiacarbocyanine perchlorate	-	0.59	OE-1 0.44	1	30	60
3,3-Diethyl-9-methyl-7,7'-bis-(dimethylamino)-thiacarbocyanine perchlorate	-	1.17	OE-2 0.97	2	40	23.7
3,3',9-Triethyl-7,7'-bis-(dimethylamino)-thiacarbocyanine perchlorate	-	1.76	OE-3 1.58	3	35	32.3

NOTE. OE-1 = Ethyl orthoformate, OE-2 = Ethyl orthoacetate, OE-3 = Ethyl orthopropionate

External Appearance of Dye	M.p.	Calculated		Found
		Formula	% N	% N
Dark red platelets	249-250°	$C_{23}H_{27}N_4S_2I$	10.18	10.16
Fine reddish-brown needles	214	$C_{24}H_{29}O_4N_4S_2Cl$	10.43	10.39
Fine green needles	216	$C_{25}H_{31}O_4N_4S_2Cl \cdot H_2O$	9.84	9.89
Dark, almost black prisms	226	$C_{25}H_{31}O_4N_4S_2Cl \cdot H_2O$	9.84	9.90
Dark brown prisms	224	$C_{26}H_{33}O_4N_4S_2Cl$	9.91	9.73
Fine, dark brown crystals	209	$C_{27}H_{35}O_4N_4S_2Cl$	9.67	9.73

in vacuum. The fraction boiling at 154-155° (6 mm) was collected. The yield was 3.13 g (63.3% of theory). Colorless oil, which rapidly crystallized. To purify it the base was crystallized from petroleum ether (yield 52% of theory). Colorless needles, m.p. 43-44°. Very easily soluble in alcohol, ether and benzene, with somewhat more difficulty in petroleum ether.

Found %: N 14.51. $C_{10}H_{12}N_2S$. Calculated %: N 14.57.

Picrate. Yellow needles, m.p. 175°. A mixture of this substance with the picrate of 5-dimethylamino-2-methylbenzothiazole (m.p. 187°) melted at 171°.

Methiodide. This was obtained in 56% yield, by heating the base with 10% excess of methyl iodide in a closed tube for 7 hours at 140-150° after gradually raising the temperature from 110° in 5 hours. Fine yellowish-green needles (from water), m.p. 188°.

Found %: N 8.20. $C_{11}H_{15}N_2SI$. Calculated %: N 8.38.

Ethiodide. Obtained in a similar manner to the previous compound. Yield 29% of theory, fine greenish-yellow prisms (from water). M.p. 182°.

Found %: N 7.98. $C_{12}H_{17}N_2SI$. Calculated %: N 8.04.

7,7'-bis-(dimethylamino)-thiacarbocyanines. The dyes were obtained by heating the methiodide or the methyl- or ethyl-p-toluenesulfonates, of 7-dimethylamino-2-methylbenzothiazole with ethyl orthocarboxylates in pyridine at 130-135° for 30-40 minutes. The methyl- and ethyl-p-toluenesulfonates of the 7-dimethylamino derivative were synthesized by heating equimolecular quantities of the base and the corresponding p-toluenesulfuric acid ester at 130-140° for 6 hours, and for obtaining the dyes these compounds were not further purified. 3,3'-Dimethyl 7,7'-bis-(dimethylamino)-thiacarbocyanine-iodide was separated from the reaction mixture in the crystalline state, and was then cooled and filtered off, washed with water and ethyl alcohol, and for purification was crystallized three times from methanol. The remaining dyestuff was precipitated from the reaction mixture with ether, dissolved in ethyl alcohol, and isolated by adding an equal volume of 10% solution of sodium chloride. To purify the dye, it was crystallized from ethyl alcohol. 3,3'-Diethyl-9-methyl- 3,3'-dimethyl-9-ethyl, and 3,3',9-triethyl-7,7'-bis-(dimethylamino)-thiacarbocyanine perchlorates were purified chromatographically in chloroform solution on aluminum oxide, and were then crystallized from ethyl alcohol. The conditions under which the dyes were obtained, their properties and the results of analysis are set forth in Table 2.

SUMMARY

1. It has been shown that, during the oxidation of m-thioacetoamino-dimethylaniline with potassium ferricyanide in alkaline solution closure of the thiazole ring occurs in the ortho position to the dimethylamino group, and 7-dimethylamino-2-methylbenzothiazole is formed.

2. The synthesis of certain 7,7'-bis-(dimethylamino)-thiacarbocyanines have been performed and the optical properties of the products studied.

3. Entry of the dimethylamino group into the 7,7' positions of thiacarbocyanines causes considerably less displacement of the absorption maximum to the longer wave portion of the spectrum, than does the entry of the same group into the 5,5'- and 6,6'- positions.

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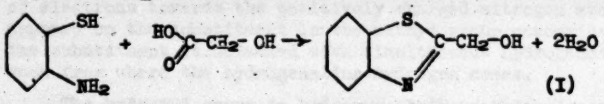
2-HYDROXYMETHYLBENZOTHIAZOLE AND ITS TRANSFORMATIONS

V. M. Zubarovsky

2-Hydroxymethylbenzothiazole (I) can serve as the starting material for the preparation of different benzothiazole derivatives; the possibility of synthesizing it is interesting. Attempts by Hoffman [1] to obtain it from o-aminothiophenol produced 3-hydroxybenzo-1,4-thiazine. There are indications [2] that 2-hydroxymethylbenzothiazole is formed as a secondary product during the interaction of benzothiazolyl-(2)-methylmagnesium bromide with acetone.

We found that 2-hydroxymethylbenzothiazole is obtained simply and in good yield by heating o-aminothiophenol in a closed glass tube with glycolic acid.



(I)

The yield is 72-76% of the theoretical. Along with the hydroxymethylbenzothiazole there is formed, in quantity of 0.5-6.0% of its weight, a secondary product melting at 306-308°, shown to be dibenzothiazolyl (II).

(II)

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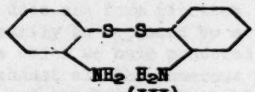
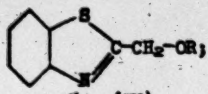


(III)

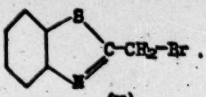
The o-aminothiophenol used for this synthesis usually contains oxidation products as impurities - o,o'-diaminodiphenyl disulfide (III); the less there is of this impurity, the less dibenzothiazole is formed by its condensation with glycolic acid. Actually, it was shown that on heating pure o,o'-diaminodiphenyl disulfide with glycolic acid under the same conditions as those prevailing in the synthesis of the hydroxymethyl compound, up to 30% of dibenzothiazolyl is formed. The mechanism of its formation is not clear.

Hydroxymethylbenzothiazole is easily freed from even small traces of dibenzothiazolyl, since the latter is practically insoluble in HCl, whereas the hydroxymethyl compound dissolves easily. The pure hydroxymethylbenzothiazole is a colorless, crystalline substance having an m.p. of 101°, possessing the properties of a heterocyclic base and of an aromatic alcohol. A peculiarity is its amphoteric character: along with the formation of salts from acids, it has the ability to dissolve in aqueous solutions of alkalies, from which crystalline alcoholates can be separated by addition of excess alkali (20% NaOH). This property permits one to speak of its "phenolic" character, and is explained by the electronophilic character of the benzothiazole nucleus. This property was utilized to obtain ethers of the substance by acting on its aqueous alkaline solutions with alkyl sulfates. We thus obtained from dimethyl sulfate and hydroxymethylbenzothiazole, the methyl ether of the latter (IV; R = CH_3), identical with the 2-methoxybenzothiazole, synthesized from o-aminothiophenol and methoxyacetic acid.

Acetyl derivatives were formed by heating hydroxymethylbenzothiazole with acetic anhydride (IV; R = $OCCH_3$).



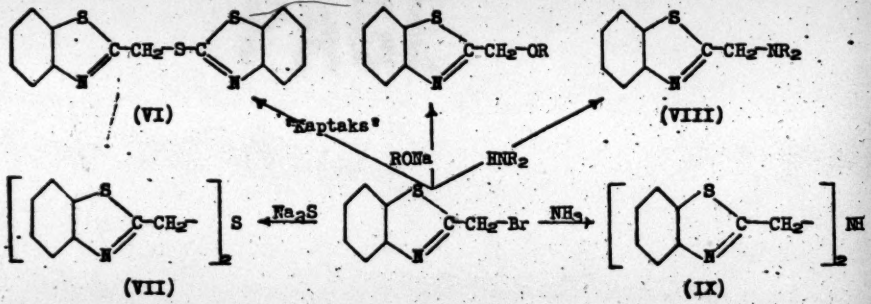
(IV)



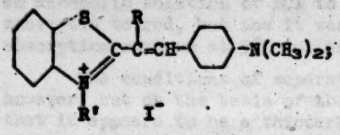
(V)

Hydroxymethyl benzothiazole and its esters and ethers (methyl and ethyl, acetyl and benzoyl derivatives) form picrates, salts with acids and quaternary salts. In the preparation of the quaternary salts, a spontaneous transformation was observed in certain cases: thus when heating the acetyl derivative with ethyl iodide in a closed tube, acetic acid was formed, and from ethoxymethylbenzothiazole (IV; R = C_2H_5) under the same conditions the ethiodide of 2-methylbenzothiazole is formed; the ethylozilate of 2-acetoxymethylbenzothiazole even splits off acetic acid when heated at ordinary pressure above 150°. The transformations referred to all involve the quaternary salts. It can be assumed that, as a result of the displacement of electrons towards the positively charged nitrogen atom, a positive charge appears on the substituent in the methyl group occupying the second position. The substituent is detached with simultaneous hydrogenation. We do not yet know from where the hydrogenating hydrogen comes.

The hydroxyl group in hydroxymethylbenzothiazole can be replaced by a bromine atom, by heating it with hydrobromic acid. 2-Bromobenzothiazole (V) is a very weak base; it does not dissolve in dilute HCl, and its hydrobromide, which may be obtained under certain conditions, is rapidly hydrolyzed by an excess of water. It does not form picrates. The bromine atom in the 2-bromine derivative may easily be replaced by a variety of other substituents; the transformations which we have produced in this direction (Scheme 1) do not by any means exhaust all the numerous possibilities. The products obtained in this manner are set forth in the table.



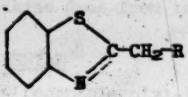
The quaternary salts of certain new derivatives of benzothiazole which we synthesized were used to obtain polymethine dyes: dimethines of the styryl type and trimethine-thiocarbocyanines. Such dyes form quaternary salts, obtained by heating 2-diethylaminomethylbenzothiazole, (VIII; R=C_2H_5) with ethyl iodide, were not, however, those expected (X and XI; R=N(C_2H_5)$_2$), but the earlier known ethiodide of 2-(p-dimethylaminostyryl)-benzothiazole having an absorption maximum at 528 mμ[3] (X; R=H; R'=C_2H_5) and bis-[3]ethylbenzothiazole-(2)]-trimethinecyanine iodide, with an absorption maximum at 558 mμ[4] (XI; R=H; R'=C_2H_5; anion=I^-); this confirms that, in the preparation of the original quaternary salt from diethylaminomethylbenzothiazole and ethyl iodide, the ethiodide of 2-methylbenzothiazole was formed, which is analogous to the formation of the quaternary salt of 2-methylbenzothiazole from its ω-substituted derivative -2-ethoxymethylbenzothiazole.

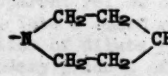
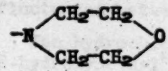
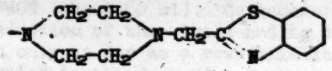
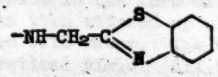


(X)

(XI)

Benzothiazolyl Amines

General Formula 

No.	R	B.p.	M.p.	M.p. of the characteristic derivative
1	$-NH-C_2H_5$	180°, 10 mm	–	Picrate, 169°
2	$-N(CH_3)_2$	146, 10 mm	–	Picrate, 154
3	$-N(C_2H_5)_2$	141, 5 mm	–	Picrate, 178
4	$-N(C_3H_7)_2$	145, 4 mm	–	Picrate, 184
5		225, 30 mm	–	Picrate, 184
6		–	71°	Picrate, 197
7		–	200	–
8		–	134	Acetyl derivative 110°

From the quaternary salts of 2-hydroxymethylbenzothiazole we hoped to obtain dyes containing chromophoric hydroxy groups in the polymethine chain (X and XI; R=OH), but we met with difficulties; as has already been explained, the salts of this nature on heating with pyridine spontaneously transform into colored substances of unknown structure. For example, the ethiodides of hydroxymethylbenzothiazole, after boiling for a short time with pyridine and subsequent decantation of the solution into water, produces a substance having a metallic luster and was shown under the microscope to be present as violet needles. This interesting transformation was not investigated further, but to prepare dyes of the type of (X) and (XI) we used the quaternary salt 2-acetoxymethylbenzothiazole (IV; R=$OOCCH_3$) from which we also obtained, in acetic anhydride solution: the ethiodide of 2-(p-dimethylamino-β-acetoxystyryl)-benzothiazole (X; R=$OOCCH_3$; R'=C_2H_5) with an absorption maximum at 498 mμ and the perchlorate of bis-[3 methyl-benzothiazole-(2)]-8,10-diacetoxytrimethinecyanine (XI; R=$OOCCH_3$; R'=CH_3) with absorption maximum at 554 mμ. If an alcoholic solution of caustic potash is slowly added to a solution of this dyestuff in ethyl alcohol, the initial violet-red coloration of the solution is converted to a blue one (absorption maximum at 606 mμ). By carefully adding

an alcoholic solution of HCl to this blue solution, the color was once again converted to red, but now it was found that the dye in solution had an absorption maximum at 565 mμ and not at 554 mμ.

The conditions of separation of this dye from solution were not found, however, but on the basis of the observations described it may be asserted that it appears to be a thiocarbocyanine with the hydroxy group in the polymethine chromophore (XI; R=OH) and the absorption maximum at 606 mμ is a characteristic of its alkali salts (XI; R=O⁻).

In conclusion the author would like to thank Prof. A. I. Kiprianov for advice about the synthesis of polymethine dyes from the quaternary salts of hydroxymethylbenzothiazole.

EXPERIMENTAL

1. 2-Hydroxymethylbenzothiazole. (Benzothiazolyl-(2)-carbinol). The method of preparation of this compound, which is described below, was the result of numerous repetitions of the synthesis of this carbinol, which itself served as the starting material for the majority of experiments.

30 g (1 mole) of o-aminothiophenol and 18.1 g (1 mole) of glycolic acid were heated in a closed glass tube: this was conveniently done by dividing the quantities between three tubes and heating for 12 hours at 130° in an oil bath. A water layer was formed. On opening the tube a very small pressure and a odor of hydrogen sulfide were observed. The contents of the tube was a transparent yellow oil, rapidly becoming transformed, when poured out of the tube, into a solid mass, which was dissolved by slightly heating it with a solution of dilute HCl (30 ml d. 1.19 HCl in 45 ml of water); the undissolved secondary product of the reaction was filtered off: its quantity was not constant, but fluctuated between 0.2 and 1.8 g.

The hydrochloric acid solution was decolorized with activated carbon and the 2-hydroxymethyl benzothiazole was precipitated from it by the addition of 20% NaOH (about 60 ml). On account of the amphoteric character of the base, the addition of the alkali had to be made with caution and the solution was taken only as far as a weak alkaline reaction. The hydroxymethyl compound separated in the form of a heavy yellow oil, solidifying into greyish-white chunks when stirred up with water. These were transferred to a filter and washed with water. The weight of the dry product was 32 g, about 75.6% of the theoretical yield. All the carbinol was crystallized from 75 ml of toluene, the crystals washed on the filter with a small quantity of cold toluene and petroleum ether. Sometimes the product had a yellowish tinge, from which it was difficult to free it even by repeated crystallization. The pure substance was obtained as fine, colorless needles melting at 101° (after 2-3 crystallizations). It had a weak odor, reminiscent of that of 2-methylbenzothiazole.

Found %: N 8.30, 8.45. C_8H_7ONS. Calculated %: N 8.48.

2-Hydroxymethylbenzothiazole dissolves well in many organic solvents; it is insoluble in cold water and has a limited solubility in hot water: it dissolves in acids and alkalies, forming alcoholates with the latter. The shaking and warming up of 1 g of the carbinol with 4 ml of 20% NaOH is sufficient to dissolve the whole of it. If the liquid becomes turbid, it can be filtered. On cooling crystals of the alcoholate separate out.

The picrate of 2-hydroxymethylbenzothiazole forms bright yellow needles, m.p. 138° (from alcohol), decomp. at 140°. The methiodide was obtained by heating 3 g of hydroxymethylbenzothiazole with 6 ml of methyl iodide for 1½ hours at 100°. Crystallized from water. After three crystallizations colorless fine needles were obtained, decomposing at 219°.

Found %: I 41.75, 41.46. $C_9H_{10}ONSI$. Calculated %: I 41.37.

The ethiodide was obtained in a similar way, by heating the base and ethyl iodide for 6 hours at 110-120°. Crystallized from water. The pure salt decomposed at 208°.

Found %: I 39.78. $C_{10}H_{12}ONSI$. Calculated %: I 39.56.

2. Identification of the side product, which was formed during the synthesis of hydroxymethylbenzothiazole. During the synthesis of hydroxymethylbenzothiazole a light yellow crystalline material separated, insoluble in dilute hydrochloric acid, and subliming on heating. This material was purified by crystallizing from a large volume of toluene. Slightly yellow crystals, with a pearly lustre were obtained, m.p. 306-308°. The substance contained nitrogen (Found %: N 10.51, 10.60) and sulfur. Fusion of the substance with KOH (1 g to 6 g KOH) at 180-200° yielded, after neutralizing the melt with hydrochloric acid, an oil (extracted with ether) giving a picrate with an m.p. of 127°, indicating o-aminothiophenol. The mixture of the substance with 2,2'-dibenzothiazole ($C_{14}H_8N_2S_2$. Calculated %: N 10.45), synthesized from o-aminothiophenol and cyanogen by Hofmann [1] melted at 306°, authentic dibenzothiazole has an m.p. of 308°.

3. 2,2'-Dibenzothiazole from o,o'-diaminodiphenyl disulfide. 2.5 g (1 mole) o,o'-diaminodiphenyl disulfide and 3 g (about 4 moles) of glycolic acid were heated together in a closed glass tube at 120-140° for 15 hours. The reaction product was treated with ether, the crystals filtered and washed with hot alcohol, acetone and ether. 0.8 g of yellow crystals were obtained. These were crystallized from toluene, using activated carbon. The purified substance, m.p. 306°, was identical with 2,2'-dibenzothiazole (by mixed m.p.'s).

4. Methylation of 2-hydroxymethylbenzothiazole with dimethyl sulfate. 5.2 g (1 mole) of hydroxymethylbenzothiazole was covered with a solution of 2 g (1.6 mole) of caustic soda in 20 ml of water, and heated until completely dissolved. The solution was cooled with ice, and when crystals of alcoholate were beginning to separate, 5.5 ml (1.3 mole) of dimethy sulfate were poured into it at once and, eliminating the external cooling of the reaction, the liquid was stirred vigorously for 10 minutes. The oil which separated was extracted with ether, the extract dried with potash, the ether distilled off and the residue distilled in vacuum at 134-135° (6 mm). The yield was 3 g, about 55% of the theoretical. The methylated product was identical with 2-methoxymethylbenzothiazole (b.p. 165° at 16 mm), synthesized by A. I. Kiprianov from o-aminothiophenol and methoxyacetic acid; it was identified by its picrate (m.p. 110°).

5. 2-Acetoxymethylbenzothiazole. 24.7 g (1 mole) of hydroxymethylbenzothiazole and 216 g (200 ml; 14 mole) of acetic anhydride were boiled together for 5 hours and then poured with stirring into 1 liter of cold water. The acetyl derivative was filtered off, and washed with water. The yield of 27 g was 87% of the theoretical. It was purified by crystallization from 60% alcohol (mother liquor decolorized with carbon) or from petroleum ether. The pure 2-acetoxymethylbenzothiazole crystallized in white needles, m.p. 78-79°.

Found %: N 6.64, 6.89. $C_{10}H_9O_2NS_2$. Calculated %: N 6.76.

From the acetoxy derivative (1 mole) and methyl iodide (6.5 mole) the iodomethylate was prepared by heating in a closed tube at 102° for 2½ hours. Colorless needles, melting at 173° (from water) with decomp.

Found %: I 36.26, 36.34. $C_{11}H_{12}O_2NSI$. Calculated %: I 36.38.

Heating the acetoxy derivative (1 mole) with ethyl iodide (5 moles) did not yield the ethiodide. Heating for 2½ hours at 100° on a water bath produced only a small quantity of product, while heating 6 hours at 110-120° caused a strong resinification; The contents of the tube had the sharp odor of acetic acid and, after separating the excess of ethyl iodide, only a small quantity of crystalline substance could be extracted from the resin with water, consisting, apparently of the impurity present in the ethiodide, namely 2-methylbenzothiazole, for on heating it with p-dimethylaminobenzaldehyde in acetic anhydride a dye was formed, with an absorption maximum at 528 mμ. The iodide of 2-acetoxy benzothiazole was obtained from its ethyl-p-toluenesulfonate and potassium iodide. The crystals were purified from 10% aqueous acetone. The ethiodide begins to decompose on heating at about 100°, and at 168-170° commences to blacken, and decompose rapidly. The ethyl-p-toluenesulfonate of acetoxymethylbenzothiazole was obtained by heating the base (1 mole) with the ethyl ester of p-toluenesulfonic acid (1.1 mole) in a closed tube at 120° for 10 hours. After three crystallizations from alcohol (carbon) the sulfonate was obtained as slightly pink needles, m.p. 188°. On heating, it decomposed at 150-170° with liberation of acetic acid.

The methylmethosulfate of acetoxymethylbenzothiazole was obtained by carefully heating it (1 mole) with freshly distilled dimethyl sulfate (4 moles) in a porcelain dish until the commencement of exothermic reaction. After the final product had been dissolved in alcohol and precipitated with ether, and afterwards crystallized from a small quantity of alcohol, it was obtained as colorless needles, m.p. 163-165°.

6. 2-Benzoylhydroxymethylbenzothiazole. 3.3 g (1 mole of 2-hydroxymethylbenzothiazole was dissolved by heating it with 9 ml of 11% aqueous caustic soda (about 1.2 mole of NaOH). 3 g (2.5 ml, 1.1 mole) of benzoyl chloride was added to the cooled solution over 2-3 minutes. The clumps of benzoyl derivative were filtered off and washed with water. Yield: 5 g recrystallized from 15 ml of alcohol (carbon). The yield after one crystallization was 3.5 g, 65% of theory; m.p. 69°. After repeated recrystallization the benzoyl derivative was obtained as colorless needles, melting sharply at 72°.

Found %: N 5.29, 5.15. $C_{15}H_{11}O_2NS$. Calculated %: N 5.20.

The methiodide, obtained by heating the benzoyl derivative with excess methyl iodide in a closed tube for 2 hours at 100°, had a decomposition temperature of 184-185°, after two crystallizations from water; it formed colorless crystals.

Found %: I 30.89, 31.08. $C_{16}H_{14}O_2NSI$. Calculated %: I 30.90.

7. 2-Bromomethylbenzothiazole. 4 g of 2-hydroxymethylbenzothiazole and 20 ml of an aqueous solution of hydrobromic acid (saturated at 0°, d. 1.78) were heated together in a closed tube in boiling water for 7 hours. It was convenient to heat a number of tubes at once, open them and unite their contents (transparent brown solution) for further treatment, which included the following (the quantities of reactants given below are for 6 tubes): they were poured into 150 ml of water, a few lumps of ice were added, and afterwards, 20% caustic soda was added to an alkaline reaction.

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1) In this operation, sometimes immediately, sometimes after a short period of waiting and stirring, a copious gray crystalline deposit of the hydrobromide of 2-bromomethylbenzothiazole separated out, which after two crystallizations from absolute alcohol, had an m.p. of 187°. This salt was immediately hydrolyzed by an excess of water. Found %: Br 50.59. $C_8H_7NSBr_2$. Calculated %: Br 50.60.

If the cooling was insufficient, an oil which, however, rapidly solidified, appeared. The product was filtered, washed with water, and treated while still damp with about 250 ml of petroleum ether at the boil (46-70°) for a certain time. After standing for a while it was cooled on ice, and the crystals filtered off, the mother liquor concentrated, and a further crop obtained from it: the general yield was 23 g, or 70% of theory. The pure substance was composed of colorless coarse needles, m.p. 45°, having a sharp odor.

Found %: Br 35.03, 34.84. C_8H_6NSBr. Calculated %: Br 35.09.

2-bromomethylbenzothiazole does not dissolve in 15% HCl, but does dissolve in the concentrated acid; it does not form a picrate, nor a quaternary salt by heating with alkyl halides or ethyl-p-toluenesulfonate.

8. 2-Alkoxymethylbenzothiazole from 2-bromomethylbenzothiazole. 2-methoxy- and 2-ethoxy-benzothiazole were synthesized from 2-bromomethyl benzothiazole and alkali methylates or ethylates. The method for these two syntheses was identical. The synthesis of 2-ethoxymethylbenzothiazolewill be described. This compound has not been reported previously. To a solution of 2.28 g (1 mole)of 2-bromomethylbenzothiazole and 5 ml of absolute alcohol, a solution of sodium ethylate was added. 0.23 g (1 gr atom) of metallic sodium in 10 ml of absolute alcohol. The mixture was boiled for 20 minutes. It was poured into 25 ml of water, extracted with ether, the extract dried with potash and the solvent distilled off. The yield was 1.2 g, 61% of theory: a yellow oily substance. After repeated distillation, 1 g of colorless liquid was obtained with an odor reminiscent of 2-methoxymethylbenzothiazole. The pure substance boiled at 279° at 752 mm and at 140° at 7 mm.

Found %: N 7.08. $C_{10}H_{11}ONS$. Calculated %: N 7.25.

2-ethoxymethylbenzothiazole, obtained in this manner, was, as expected, identical with the product of condensing aminothiophenol with ethoxyacetic acid. This condensation was achieved by heating 5 g (1 mole)of o-aminothiophenol with 5.58 g (1.1 mole)of ethoxyacetic acid in a closed glass tube for 10 hours at 135°. 4.1 g of thiazole were obtained, 58% of the theoretical yield. It boiled at 232° (766 mm), and after repeated distillation, at 141° (at 6-7 mm).

The action of ethyl iodide on 2-ethoxymethylbenzothiazole did not produce the ethiodide: 1.93 g (1 mole)of the 2-ethoxy compound and 18.72 g (9.7 ml, 12 moles ofethyl iodide were heated in a closed glass tube for 4 hours at 140°. After separating the excess of ethyl iodide, the dark resinous mass was extracted with hot water. The aqueous extract was decolorized and evaporated, when the main quantity of the quaternary salt separated out: a further quantity was obtained from the mother liquor. In all 0.4 g,m.p. 199°. A mixture of the salt and the authentic ethiodide of 2-methylbenzothiazole melted at 198°. A dye was obtained from the salt and p-dimethylaminobenzaldehyde: this was a styryl with an absorption maximum at 528 mμ (in ethyl alcohol).

In the synthesis of 2-methoxymethylbenzothiazole and 2-bromomethylbenzothiazole, 1.95 g of the first, or 81 % of theory was obtained. Methoxymethylbenzothiazole boils at 268-269° (767 mm) and crystallizes on cooling; the crystals, washed with petroleum ether, had an m.p. of 36°. The picrate of 2-methoxymethylbenzothiazole was obtained by heating equivalent quantities of the base and picric acid in a closed tube until complete solution had been attained.. The picrate melted at 111° (from crystallized chloroform).

The ethiodide of 2-methoxymethylbenzothiazole melted at 158-160° and decomposed at 164°.

9. Bis-benzothiazolyl-(2)-sulfide (VII). 2.28 g (2 moles) of 2-bromomethylbenzothiazole was added to a suspension of 0.9 g (1.1 mole) of anhydrous sodium sulfate in 40 ml of ethyl alcohol, and the mixture was boiled for 40 minutes. The yellow crystalline deposit was filtered off and thoroughly washed with water. The yield was 1.35 g, or 82.3% of theory. After crystallization from alcohol (using activated carbon) it was obtained as colorless shining crystals, m.p. 119-121°.

Found %: N 8.33. $C_{16}H_{12}N_2S_3$. Calculated %: N 8.54.

10. 2-Benzothiazolyl-(2)-methylmercaptobenzothiazole (VI). 2.4 g (1 mole) of "Captax" (2-mercaptobenzothiazole), crystallized from toluene, was heated with a solution of 1 g (1.3 mole) of caustic potash in 30 ml of alcohol. A hot solution of 3.3 g (1 mole) of 2-bromomethylbenzothiazole in 7 ml of alcohol was added to it. The mixture was boiled for one hour, cooled, the crystalline deposit was filtered off and washed with water and alcohol. After crystallizing from dilute alcohol, a yield of 2.5 g, or 55% of theory, was obtained. Yellowish white crystalline powder, m.p. 101-102°.

Found %: N 8.84, 9.19. $C_{15}H_{10}N_2S_3$. Calculated %: N 8.92.

11. Bis-benzothiazol (2)-methyl-amine (No. 8 on the table). 2.28 g of 2-bromomethylbenzothiazole was covered with a mixture of 10 ml of 20% aqueous ammonia and 15 ml of ethyl alcohol. The mixture was boiled for 15 minutes and 15 ml of liquid was distilled off from it; crystals, or an easily crystallized oil, separated. The product was washed with water, 15% aqueous potash, and again with water. The yield was 0.75 g, or 48% of theory. The moist amine was dissolved in benzene, (6 ml for 1 g), the solution decolorized with carbon, an equal volume of ether added to it and the mixture cooled; the amine crystallized in colorless needles, melting at 128-132°. After repeated crystallization a substance with an m.p. of 134° was obtained.

Found %: N 13.24, 13.35, 13.50. 0.0520 g subst.; 0.6470 g camphor: Δt 10.0°. Found: M 321.5. $C_{16}H_{13}N_3S_2$. Calculated %: N 13.50; M 311.0.

The acetyl derivative of dibenzothiazolyamine was obtained by boiling it (1 mole) with an excess of acetic anhydride (50 moles) for 3.5 hours. It was crystallized from a mixture of benzene and petroleum ether, or from a large quantity of water. M.p. 110° (from benzene).

12. 2-(Ethylaminomethyl)-benzothiazole (No. 1 in the table). A solution of 2.3 g (1 mol 2-bromomethylbenzothiazole in 20 ml of dry ether was poured rapidly, with cooling, into a solution of 4.5 g (6.3 ml, 10 moles) of dry ethylamine in 15 ml of ether. It was boiled for five minutes, when crystals or a viscous congealing mass of ethylamine hydrobromide separated, which was filtered off after 1/2 hour (1 g, m.p. 158°). The solvent excess was distilled off from the filtrate, and the excess of ethylamine and the residue were distilled over in vacuum, The main bulk of the product distilled over at 180° under 10 mm. The yield was 1.5 g, about 75% of the theoretical. A picrate, melting at 169° (from alcohol), was obtained. The picrate was analyzed.

Found %: N 16.48, 16.37. $C_{16}H_{15}O_7N_5S$. Calculated %: N 16.63.

13. 2-(Dimethylaminomethyl)-benzothiazole (No. 2 in the table). The method of synthesizing this differed little from the preceding: a mixture of 4 g of 2-bromomethylbenzothiazole, 33 ml of a 33% solution of dimethylamine in absolute alcohol, and 20 ml of absolute alcohol, were boiled together. The solvent was distilled off until the volume of the residue reached 12 ml. This residue was poured into 25 ml of dry ether, in order to precipitate the dimethylamine hydrobromide, which

was filtered off. The amine which had been synthesized was isolated from the filtrate. It was a colorless liquid with a weak amine-like odor, boiling at 146° at 10 mm. The yield was 2.2 g, or 66.5% of theory. The picrate of the base melted at 154° (from alcohol). The picrate was analyzed.

Found %: N 16.13, 16.38. $C_{10}H_{15}O_7N_5S$. Calculated %: N 16.63.

14. 2-(Diethylaminomethyl)-benzothiazole (No. 3 in the table). The method for synthesizing this was similar in every way to that employed for No. 12 above. The yield was about 75% of theory. The freshly distilled amine was a colorless liquid with a scarcely perceptible odor, almost insoluble in water. d^{20} 1.08, b.p. 141°/5 mm.

Found %: N 12.62, 12.40, 13.02. $C_{12}H_{16}N_2S$. Calculated %: N 12.73.

The amine formed a picrate of m.p. 178° (from alcohol).

Found %: N 15.35. $C_{18}H_{18}O_7N_5S$. Calculated %: N 15.59.

By passing dry HCl gas through a solution of the amine in absolute alcohol, the amine hydrochloride was formed, in colorless crystals of m.p. 119-120° (from absolute alcohol).

Found %: Cl 23.82. $C_{12}H_{18}N_2SCl_2$. Calculated %: Cl 24.23.

Attempts were made to prepare quaternary salts of the amine. 1.1 g (1 mole) of the amine and 0.86 g (1.1 mole) of ethyl iodide were heated in a closed tube for 6 hours at 135°. The dark viscous mass obtained was mixed with 30 ml of hot water, and the insoluble part extracted with toluene. The aqueous solution was decolorized with carbon and evaporated, and the residual water was removed in a vacuum dessicator. Light brown crystalline mass (1 g), utilized for obtaining a dye (a styryl from p-dimethylaminobenzaldehyde) and thiocarbocyanine (from the ethyl ester of orthoformic acid). The first had an absorption maximum at 528 mμ (in ethyl alcohol), and the second had one at 558 mμ (from alcohol).

15. 2-(Dipropylaminomethyl)-benzothiazole (No. 4 in table). The synthesis was similar to that of the previous amine. 4.6 g (1 mole) of 2-bromomethylbenzothiazole and 5.0 g (2.5 moles) dipropylamine in dry ether were heated together for 1/2 hour. After distilling off the ether, the dipropylamine hydrobromide gradually separated and was filtered off (m.p. 268°). The yield of the main product was 3.0 g, or 60% of theory, after one distillation in vacuum. B.p. 145/4mm. The pure amine was a colorless, odorless, thick liquid.

Found %: N 11.14. $C_{14}H_{20}N_2S$. Calculated %: N 11.29.

The picrate of the base melted at 105° (from alcohol). In its preparation its considerable solubility in alcohol must be taken into account.

16. N-Piperidylbenzothiazolyl(2)-methane (No. 5 in the table). The method of synthesis was the same as in the two preceding cases. The yield of piperidylbenzothiazolylmethane, after distillation in vacuum, was 60% of theory. B.p. 225/30 mm. The liquid, after distillation, crystallized rapidly. After further purification by crystallization from 60% alcohol it was obtained as colorless crystals, m.p. 53°.

Found %: N 11.80. $C_{13}H_{16}N_2S$. Calculated %: N 12.07.

In obtaining the picrate, either equivalent quantities of the base and picric acid, or an excess of the latter (2-3 moles) gave one and the same picrate, difficultly soluble in hot alcohol, m.p. 184° (from alcohol).

17. N-Morpholylbenzothiazolyl-(2)-methane (No. 6 in the table). 4.6 g (1 mole) of 2-bromomethylbenzothiazole, 3.6 g (2 moles) of morpholine and 40 ml of dry ether were boiled together, with vigorous stirring, for 1/2 hour. The product was separated according to the procedures outlined in Expts. Nos. 12 and 14. The moist product, after separation from its ethereal solution, solidified: the yield was 65% of the theoretical. After crystallizing from petroleum ether (32 ml per g), 2 g of a colorless product was obtained, crystalline and odorless, m.p. 71°.

Found %: N 11.76. $C_{12}H_{14}ON_2S$. Calculated %: N 11.97.

The picrate of the base was not very soluble in water, not even in boiling water (1 g in 550 ml): m.p. 197° with decomposition. On heating the free base in a closed tube with an excess of methyl iodide at 100° for 1/2 hour, the methiodide was formed, which was washed with acetone and crystallized from 75% aqueous alcohol. Fine, snow white needles. M.p. 188°.

Found %: I 33.79, 33.90. $C_{13}H_{17}ON_2SI$. Calculated %: I 33.78.

18. N,N'-Bis-benzothiazolyl-(2)-methyl-piperazine (No. 7 in the table). A hot solution of 3.5 g of 2-bromomethylbenzothiazole in 5 ml of alcohol, and 5.5 g of piperazine in 10 ml of alcohol, were mixed and boiled for 10 minutes. The deposit was filtered off and washed with ether and alcohol. Yield 1 g, colorless crystals, m.p. 200° (from xylene).

Found %: N 14.22, 14.31; S 16.59. $C_{20}H_{20}N_4S_2$. Calculated %: N 14.74; S 16.84.

The substance which remained in the mother liquor was not examined.

19. Action of pyridine on 2-hydroxymethylbenzothiazole ethiodide. When 2-hydroxymethylbenzothiazole ethiodide was mixed with pyridine in the cold, a brownish violet coloration appeared, which became intense on heating, but disappeared in a few minutes when the solution was boiled. To isolate the substance causing the color, the mixture of ethiodide and pyridine was brought 2 to 3 times to the boil, and then diluted with a large quantity of water; the substance separated in the form of minute blue needles, agglomerated into flocs; the properties of the substance were not examined.

20. 2-p-Dimethylamino-β-acetoxystyryl-benzothiazole ethiodide (X; R = $COCH_3$; R' = C_2H_5). 2.05 g (1 mole) of ethyl-p-toluenesulfonate of 2-acetoxymethylbenzothiazole, 0.75 g (1 mole) of p-dimethylaminobenzaldehyde in 10 ml of acetic anhydride were boiled together for 45 minutes. The solution of the dyestuff formed was poured into a hot solution of 5 g of KI in 75 ml of water. The solution was cooled and the crystals of dyestuff were filtered off, thoroughly washed on the filter with cold and warm water, alcohol and ether. The yield of 1.78 g was 70.8% of theory. The dyestuff, crystallized from a large quantity of alcohol, was obtained in the form of fine, violet, lusterless needles, m.p. 184°, and absorption maximum at 498 mμ (in alcohol).

Found %: I 25.61, 25.46. $C_{21}H_{23}O_2N_2SI$. Calculated %: I 25.71.

21. B is [3-methylbenzothiazole-(2)]-8,10-diacetoxytrimethinecyanine perchlorate (XI; R = $OCCH_3$; R' = CH_3). 1.75 g (2 moles) of the 2-acetoxymethylbenzothiazole ethiodide, 1.5 g (4 moles) of ethyl orthoformate in 10 ml of acetic anhydride, were boiled together for 30 minutes. The mixture was poured into a hot solution of 1 g of sodium perchlorate in 50 ml of water. The dyestuff separated out as a viscous mass, solidifying when stirred with water. The moist dye (0.7 g, 50% of theory) was pulverized and treated for a certain time with ether,

and then crystallized from alcohol, from which the first portion separated in the form of very fine crystals of insufficient purity: these were filtered off and, adding ether to the mother liquor, the pure dye was obtained as a black-violet powder, decomp. at 178°.

Found %: Cl 6.21, 6.36. $C_{23}H_{21}O_8N_2S_2Cl$. Calculated %: Cl 6.43.

The absorption maximum for the dye was at 554 mμ (in alcohol). Some of the violet-red solution was placed in a spectrographic cuvette in which the determination of the position of the absorption maximum was made; to this was added, with a microcapillary, an alcoholic solution of KOH until the red color was turned to blue; it was then found that the absorption max. was shifted to 606 mμ. Finally, alcoholic HCl was carefully added to the blue solution. The blue color turned red: the absorption maximum for the dyestuff absorbing light in this solution was found to be at 565 mμ.

SUMMARY

1. It has been shown that condensation of glycolic acid with aminothiophenol yields 2-hydroxymethylbenzothiazole in good yield: the synthesis of the simplest alcohol of the benzothiazole series had not been previously described. The properties of 2-hydroxymethylbenzothiazole were studied and a number of its derivatives were prepared.

2. 2-Hydroxymethylbenzothiazole is easily converted to 2-bromomethylbenzothiazole by the action of hydrobromic acid; this bromo-compound served as the starting point for the synthesis of numerous derivatives of 2-methylbenzothiazole with different substituents in the methyl group. A series of new derivatives of this type was obtained.

3. The spontaneous transformation of quaternary salts of certain ω-substituted 2-methylbenzothiazoles, into the quaternary salts of 2-methylbenzothiazole, was observed.

4. New dyes were synthesized from the quaternary salts of the acetyl derivatives of 2-hydroxy-methylbenzothiazole; a) dimethinestyryl type-2-[p-dimethylamino-β-acetoxystyryl]-benzothiazole ethiodide and b) trimethinethiocarbocyanines, bis-β-methylbenzothiazole-(2)]-8,10-diacetoxytrimethinecyanine perchlorate. The transformations of the latter under the influence of alkalies were studied. The optical properties of the dyestuffs named, and of bis-β-methylbenzothiazole-(2)]-8, 10-dihydroxytrimethinecyanine, formed from thiocarbocyanine under the influence of alkalies were investigated.

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SYNTHESIS OF 2-ALKYL-α-NAPTHOTHIAZOLES. II

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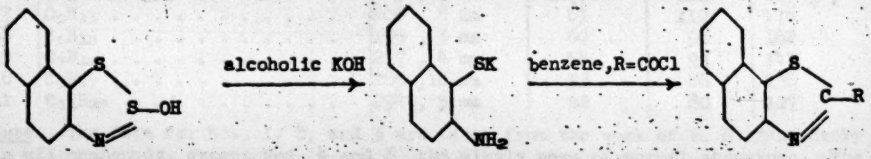
One of us has proposed a convenient method for the synthesis of 2-alkyl-α-naphthothiazole consisting in the preparation of the potassium salt of 2-amino-1-thionaphthol by cleavage of 1,2-naphthalenethiazthionene-hydrate with an alcoholic solution of potassium hydroxide, and the condensation of this salt with the anhydrides or acid chlorides of [1] monobasic fatty acids. Considerable quantities of 2-methyl-2-ethyl- and 2-propyl-α-naphthothiazoles were thus obtained, and the properties of the last two, not previously described, were studied.

By using the method referred to we synthesized a number of new 2-alkyl-α-naphthothiazoles, and certain of their derivatives. Since the fatty acid chlorides are in many cases more accessible than the anhydrides, we utilized them exclusively. Thus, in the work referred to, the following scheme was followed for the synthesis of 2-alkyl-α-naphthothiazoles:



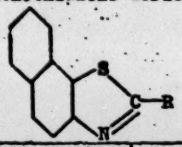
Cleavage of 1,2-naphthalenethiazthionine hydrate with alcoholic solutions of alkalies was induced as mentioned above, but the condensation of the potassium salt of 2-amino-1-naphthol with the acid chloride was brought about by heating the salt with a solution of the acid chloride in dry benzene. From the acid chlorides of isobutyric, valeric, isovaleric (isopropylacetic), caproic, heptoic, caprylic, pelargonic, and lauric acids we obtained 2-alkyl-α-naphthothiazoles, containing the following alkyl groups: butyl, amyl, hexyl, octyl and undecyl; the constants of these are set forth in Table 1.

The new 2-alkyl-α-napththothiazoles, in which the alkyl radicals are normal ones are colorless crystalline compounds, which do not darken on storing after thorough purification. 2-Isopropyl- and 2-isobutyl-α-napthothiazoles are colorless liquids, which darken considerably on heating and which boil at lower temperatures than the corresponding compounds containing the normal radicals. Among the latter there was observed a progressive rise of b.p. in going from the lower to the higher homologs. The plot of the m.p. against number of C atoms in the alkyl radical is periodic, the maxima increasing as the series is ascended. Well purified 2-alkyl-α-naphthothiazoles, at ordinary temperature, either have no odor, or else they have a pleasant "thiazole" odor; their solubility in the majority of organic solvents is considerable; the solid homologs crystallize well from alcohol. The lower homologs dissolve easily in hydrochloric acid, the higher ones with more difficulty; all derivatives on heating with methyl or ethyl iodides form alkylhalogenates whose rate of formation is greater for the lower homologs. The methiodides crystallize well from water or alcohol, in the form of colorless, needle-shaped crystals, whose m.p. gradually decreases as the series is ascended from the lower to higher homologs (Table 1). The same correlation can be observed with the picrates, which are easily formed by mixing together hot alcoholic solutions of the alkylnaphthothiazoles and of picric acid.

Table 1

Homologs of the 2-Alkyl-α-naphthothiazole Series

General formula



No.	R	Constants of the thiazole		M.p. of the picrate	M.p. of the methiodide
		b.p.	m.p.		
1	CH_3	173°, 5 mm	47°	172.5°	--
2	C_2H_5	164, 3 mm	25	183	216 [1]
3	C_3H_7	179, 4 mm	23	182	213 [1]
4	$CH(CH_3)_2$	160, 5 mm	Liquid	184	209 [1]
5	C_4H_9	186, 5 mm	50	156	195 [1]
6	CH_2-$CH(CH_3)_2$	163, 7 mm	Liquid	181	213 [1]
7	C_5H_{11}	208, 8 mm	61	119	176
8	C_6H_{13}	195, 3 mm	60	96	162
9	C_7H_{15}	217, 4 mm	54	93	147
10	C_8H_{17}	285, 10 mm	53	86	136
11	$C_{11}H_{23}$	294, 5 mm	62	80	127

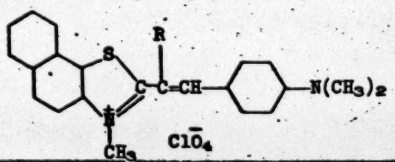
Note. The data for Nos. 1, 2, and 3 are taken from the work of V. M. Zabarovsky [1]. In all compounds, except Nos. 4 and 6, the alkyls were of normal structure. The references [1] denote a coincidence of melting and decomposition.

From the methiodides of 2-alkyl-α-naphthothiazoles and p-dimethylaminobenzaldehyde there are formed, in general under similar conditions of synthesis, dimethine dyes of the styryl type: however, these dyes can more conveniently be obtained from methyl methosulfates, since in this way a higher rate of formation and a better yield are secured. In Table 2 the structures of the dyes which we synthesized are set forth, together with some data about their properties.

Table 2

Dyes, Methylperchlorates of 2-(p-Dimethylamino-β-alkyl-styryl)-α-Naphthothiazoles

General formula



No.	R	M.p.	Absorption maximum (in mμ)	Color of the crystals (from alcohol)
1	$CH(CH_3)_2$	215°	450°	Reddish-brown
2	C_3H_7	205	473	Dark red
3	C_4H_9	196	471	Dark red
4	C_5H_{11}	170	470	Light red
5	C_6H_{13}	160	471	Red-orange
6	C_7H_{15}	158	471	Orange

Note. In all dyes except No. 1, the alkyl radicals were normal. The absorption maxima for the dyes were determined in alcoholic solution.

The data relative to the absorption maxima supplement the earlier observation

[1], that in this series of dyestuffs there is a color deepening in going from the derivatives in which the methine group chromophore contains no substituents (formula in Table 2; R=H) having an absorption maximum at 537 mμ to those in which this chromophore is alkyl-substituted (R=alkyl in the formula of Table 2). In addition, it has been shown here that dyes in which the alkyl group is a branched-chain one, have a deeper color than those in which the alkyl group is the corresponding normal isomer (cf. absorption maxima for Compounds 1 and 2 in Table 2). Observation of the change in color of styryl dyes, caused by the introduction of different alkyl groups into the β-position in the methine chromophore, were in agreement with the opinions about the relation between the color of dyes and their steric configuration, developed by Kiprianov and Ushenko [2].

The 2-alkyl-α-naphthothiazoles described in this paper were not used for the synthesis of cyanine dyes. Such dyes had been obtained previously from 2-methyl-, 2-ethyl-, and 2-propyl-α-naphthothiazoles, but the methyl methosulfates of 2-butyl- and 2-isobutyl-α-naphthothiazoles, even on prolonged boiling with ethyl orthoformate in pyridine, gave only traces of dyes.

EXPERIMENTAL

1. Synthesis of 2-alkyl-α-naphthothiazoles (general method). The preparation of the potassium salt of 2-amino-1-thionaphthol by cleavage, in alcoholic potash, of 1,2-naphthalene thiazthionine hydrate was made, following Zubarovsky [1]. It is convenient to start with 22.1 g of the latter compound (1 mole). After carefully removing traces of ethyl alcohol in vacuum, the reactor was provided with a reflux condenser and, to the molten potassium salt of 2-amino-1-thionaphthol, a benzene solution of the acid chloride (1.2--1.5 moles) of a monobasic fatty acid (2--2.5 ml of benzene per g of acid chloride) was added.

In certain cases we used a considerable excess of acid chloride (2.5 moles) but this did not have any considerable effect upon the yield of thiazole. If, after the addition of the benzene solution of the acid chloride, exothermic reaction did not set in immediately, then the mixture was heated a little. When the exothermic reaction had finished, the mixture was boiled for 1½ hours, after which 1½ or 2 volumes of water and 20% caustic soda or potash to an alkaline reaction, were added with stirring. The benzene layer was separated, the aqueous layer extracted with benzene and the united benzene solutions were dried with potash; the solution was filtered, the benzene distilled off, and the residue twice distilled in vacuum (5-6 mm). The yield of thiazole; after the double redistillation, was 36-50% of the theoretical. The solid thiazoles, where convenient, were subjected to further purification by crystallizing them from a considerable quantity of ethyl alcohol.

Table 3

Yield of 2-Alkyl-α-Naphthothiazoles and Results of Their Analysis

No.	Empirical formula	Yield of thiazole (in %)	N content (in %)	
			Found	Calculated
4	$C_{14}H_{13}NS$	38	6.13, 6.07	6.18
5	$C_{15}H_{15}NS$	39.5	5.83, 5.88	5.81
6	$C_{15}H_{15}NS$	41.5	5.70, 5.77	5.81
7	$C_{16}H_{17}NS$	36	5.57, 5.69	5.49
8	$C_{17}H_{19}NS$	50	5.39, 5.49	5.20
9	$C_{18}H_{21}NS$	37	4.99, 4.93	4.95
10	$C_{19}H_{23}NS$	45	4.73, 4.83	4.71
11	$C_{22}H_{29}NS$	36.5	4.10, 4.24	4.13

Note. In this Table, and in Table 1, the same numbers are used to identify the same thiazole. The nitrogen was determined by Dumas method (micromethod).

Picrates. The thiazole picrates were obtained by heating, in alcoholic solution, equimolecular quantities of thiazole and picric acid: the thiazole was dissolved in 3-4 times the quantity of alcohol, and the picric acid in 7-8 times. The crystalline precipitate of picrate was separated immediately, or else after standing some time. The picrates crystallized well from ethyl alcohol.

Methiodides. The methiodides were formed by heating the 2-alkyl-α-naphthothiazoles (1 mole) with an excess (8 moles) of methyl iodide in a closed tube for 5-8 hours at 100°. A longer period of heating was required for homologs containing 7 or more C atoms in the alkyl group. The crude methiodides were washed with ethyl acetate or acetone, followed by ether, and crystallized from water or alcohol. The latter was used for crystallizing the methiodides of 2-alkyl-α-naphthothiazoles containing 5 or more C atoms in the alkyl group. The ethiodides were obtained in the same way.

2. Synthesis of dyes of the styryl type from the quaternary salts of 2-alkyl-α-naphthothiazoles and p-dimethylaminobenzaldehyde. Methylmethosulfates. The methylmethosulfates of 2-alkyl-α-naphthothiazoles were obtained by heating a mixture of the base (1 mole) with freshly distilled dimethyl sulfate (1.5 mole): external heating was required at first, until exothermic reaction started, and after the latter had ceased, the mixture was heated for 15 minutes over boiling water. The reaction product was dissolved by heating with a 5-6 fold quantity of alcohol and the methylmethosulfate was separated by adding ether to its warm alcoholic solution until turbidity commenced; the mixture was cooled on ice, the quaternary salt filtered off and washed with ether. The methylmethosulfates of the lower homologs separated in the crystalline form (colorless needles), the higher ones as thick crystallizing masses. The quaternary salts were used for the synthesis of the dyes without further purification, after drying in a vacuum dessicator over sulfuric acid.

Dyes. A mixture of the 2-alkyl-α-naphthothiazole methylmethosulfate (1 mole), p-dimethylaminobenzaldehyde (1 mole) and acetic anhydride (4 ml/g of methylmethosulfate), was boiled in a flask under reflux for 25 minutes. The warm solution of the dyestuff formed was poured into a hot solution of sodium perchlorate (2 moles) in water (35-40 ml g of perchlorate). The dye separated as an oily mass, which gradually solidified (in the case of dyes Nos. 4 and 6, Table 4, only after some hours or after washing with warm benzene followed by ether). The lumps of dyestuff were broken up in a mortar with a small quantity of alcohol, filtered and washed with water, alcohol and ether successively; the yield of dyestuff, after such treatment, varied between 53 and 84% of theory. For the study of the optical properties, determination of the physical constants and analysis, the dyes were crystallized 2-3 times from alcohol; the solutions were filtered hot.

SUMMARY

1. Eight new homologs of the 2-alkyl-α-naphthothiazoles have been synthesized, containing the following alkyl groups: isopropyl, isobutyl, normal butyl, amyl, hexyl, heptyl, octyl and undecyl. The properties of these thiazoles have been studied and a series of their salts obtained.

2. From the quaternary salts of these new 2-alkyl-α-naphthothiazole compounds, and p-dimethylaminobenzaldehyde, styryl-type dyes were obtained, whose optical characteristics were investigated.

Table 4

Yield of Dyes and Results of Analysis

No.	Empirical Formula	Yield of dyestuff	Chlorine Content (in %)	
			Found	Calculated
1	$C_{25}H_{27}O_4N_2SCl$	53	7.31, 7.40	7.30
2	$C_{25}H_{27}O_4N_2SCl$	56	7.36, 7.55	7.30
3	$C_{26}H_{29}O_4N_2SCl$	60	7.28, 7.22	7.09
4	$C_{27}H_{31}O_4N_2SCl$	80	6.67, 6.72	7.90
5	$C_{28}H_{33}O_4N_2SCl$	73	6.60, 6.89	6.72
6	$C_{29}H_{35}O_4N_2SCl$	84	6.66, 6.84	6.54

NOTE. In this Table and Table 2, the same dye has the same number. The chlorine was determined by Carius' Method (micromethod).

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1) See Consultants Bureau English translation, p. 139.

SYNTHESIS OF STRUCTURAL FRAGMENTS OF ROTHENONE AND OF ITS CONGENERS

II. SYNTHESES IN THE FIELD OF TUBAIC ACID

A. A. Shamshurin

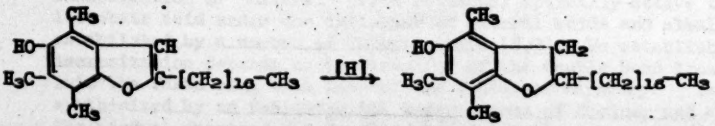
In the previous paper [1] we gave a description of the synthesis of certain substituted derivatives of 4-hydroxy coumarone, namely, 2-acetyl-4-hydroxy-5-carbomethoxy-coumarone, 2-acetyl-4-hydroxy-coumarone. We found that they could be used as the starting materials for the synthesis of tubanol and tubaic acid, which are products of the alkaline cleavage of rotenone[1], known as an insecticide of vegetable origin. Tubanol (VIII) and tubaic acid (IX) contain the isopropenyl group substituted in the 2-position of the hydrogenated ring of 4-hydroxy-coumarone, i.e., 4-hydroxy-coumaran and, consequently, the next stage in the synthesis of these compounds should be a hydrogenation, and this we accordingly performed.

The first project – to hydrogenate the double bonds in the furan ring of 4-hydroxy-coumarone with the aid of sodium amalgam in alcoholic-acetic acid solution, was not carried to a conclusion, in view of the serious resinification which occurred in the reduction of the initial 2-acetyl-4-hydroxy-coumarone, although there are descriptions in the literature of successful results in certain similar cases [3]. It is generally known that the furan system hydrogenates less easily than the carbonyl group, and, for example, the hydrogenation of 2-acetyl-benzofuran with platinum, as Shriner and Anderson have shown [4], gives the alcohol 2-(1-hydroxyethyl)-benzofuran. Reduction of the original product on Raney nickel is complete and yields the saturated alcohol 2-(1-hydroxyethyl)-dihydrobenzofuran.

We decided to carry out the catalytic hydrogenation and, in the search for suitable selective catalysts came upon palladized carbon.

We followed the work of a number of authors who have studied the chemical nature of vitamin E, and in particular, the data of Bergel and co-workers [5] obtained in the experimental determination of the structure of α-tocopherol. These investigators demonstrated the possibility of partially hydrogenating 5-hydroxy-4,6,7-trimethyl-2-n-heptadiene-coumarone (Ia) to the corresponding coumaran (Ib) with the catalyst mentioned.

The hydrogenation proceeded very easily according to the scheme:

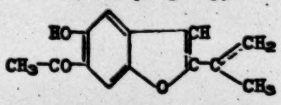


(Ia) (Ib)

Apart from this, other authors easily hydrogenated derivatives of coumarone in the same way, euparin (II), from Eupatorium purpureum, to tetrahydroeuparin. The hydrogenation in this case was selective, the carbonyl of the acetyl group attached to the benzene nucleus not being hydrogenated on palladized carbon.

[1] For a short review of the question of rotenone and its synthesis, see our papers [1,2].

Euparin, as can be seen from its structure (II), approximates to our compound in that it contains an acetyl group, and also has a double bond in the furan ring:



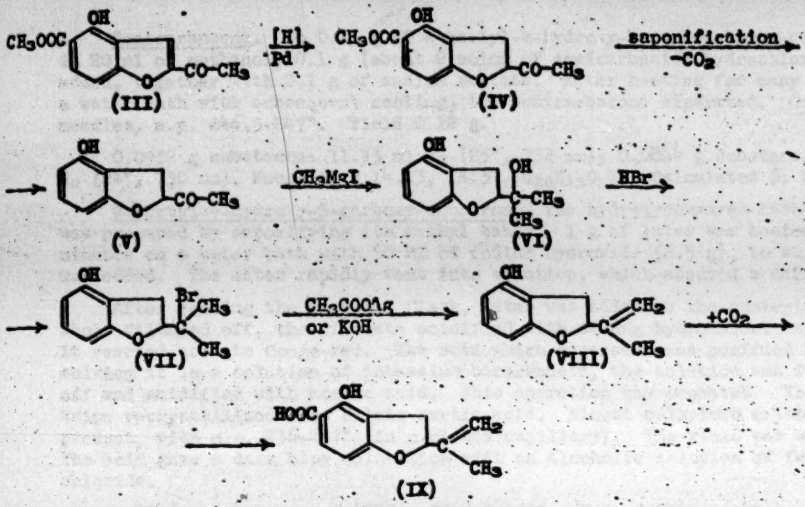
(II)

The projected scheme for the synthesis of tubaic acid passes through a Grignard stage. Hence we decided to eliminate one of the three functional groups in 2-acetyl-4-hydroxy-5-carbomethoxycoumaran, each of which is capable of interaction with a Grignard reagent. This was in contradiction to our first intention, as expressed in our first communication. We eliminated the ester group by saponification and decarboxylation. Furthermore, we obtained by the Grignard reaction the corresponding alcohol (VI) which was converted to the bromide (VII). In experiments to obtain, in order to identify the bromide, the acetate of the original alcohol by treatment of the bromide with silver acetate, we obtained tubanol (VIII) in place of the expected ester, as under these conditions the elements of HBr are easily split off from the bromide. This ability of silver acetate to act as a dehydrobromination reagent has been noted by a number of authors [7], in connection with the synthesis of certain benzene derivatives, structurally similar to penicillic acid. For example:

Treatment of the bromide with alcoholic alkali also yielded tubanol. To convert tubanol to tubaic acid (IX), it was carboxylated with solid carbon dioxide under the conditions described in Communication I, similar to those for the conversion of 2-acetyl-4-hydroxy-coumarone to the corresponding o-phenolcarboxylic acid.

For purposes of identification, part of the tubaic acid obtained was isomerized into the optically inactive isotubaic acid. The fact of the isomerization of "natural" (from rotenone) optically active tubaic acid into isotubaic acid under the influence of mineral acids and alkalies has been established by a number of investigators [8,9]. We established that this isomerization depends on the transfer of the double bond from the side chain into the furan ring with loss of the center of asymetry. Isotubaic acid was synthesized by us following the descriptions of Shriner and Witte [10], and the product obtained and found to be identical with ours. Besides this, tubaic acid was analyzed, its cesium salt being obtained, and small samples of it were oxidized with potassium permanganate. While oxidation of isotubaic gave isobutyric acid under these conditions, tubaic acid itself only gave acetic acid, thanks to the presence of the isopropenyl radical. The acetic acid was qualitatively determined by the lanthanic test.

The complete method of synthesis of tubaic acid can be compressed into the following scheme:



EXPERIMENTAL

2-Acetyl-4-hydroxy-5-carbomethoxycoumaran (IV). To hydrogenate the double bond in the furan ring we used palladized activated carbon. The carbon was shaken up in the hydrogenation vessel with an aqueous solution of palladium chloride to complete saturation in an atmosphere of hydrogen. The C:$PdCl_2$ ratio was 1:10. The catalyst was allowed to settle out, washed with water, alcohol, and after final drying in a dessicator over aluminum oxide, was used for reaction. The hydrogen was purified by passage through alkaline pyrogallol, a solution of sodium hydrosulfite and was then dried with calcium chloride and soda lime.

1 g of 2-acetyl-4-hydroxy-5-carbomethoxy-coumarone (III), melting at 178-179°, was hydrogenated in 85 ml of ethyl acetate on palladized carbon (0.2 g $PdCl_2$ on 2 g of carbon) at normal atmospheric pressure. After 1½ hours the absorption of hydrogen had ceased, the amount absorbed being approximately 1 mole. The catalyst was filtered off, the solvent distilled off, and the dihydro-derivative was twice recrystallized from gasoline (70-90° fraction). Colorless needles, m.p. 182-183°. Yield 0.82 g.

0.1771 g substance: 0.3789 g CO_2; 0.0920 g H_2O; 0.2114 g substance; 0.4529 g CO_2; 0.0930 g H_2O. Found %: C 58.36, 58.44; H 4.94, 4.89. $C_{12}H_{12}O_5$. Calculated %: C 58.53; H 4.87.

Acetate. 0.25 g of the previous compound was mixed with an excess of acetic anhydride and 5 ml of dry pyridine, the mixture was allowed to stand at room temperature for two days, and was finally heated for a few minutes on a water bath. The acetate was precipitated by addition of water and after drying in a dessicator over calcium chloride, was recrystallized from gasoline as colorless needles, m.p. 163-164°.

0.1442 g substance: 0.3186 g CO_2; 0.0667 g H_2O; 0.1165 g substance: 0.2242 g CO_2; 0.0540 g H_2O. Found %: C 60.26, 60.31; H 5.14, 5.15. $C_{14}H_{14}O_6$. Calculated %: C 60.43; H 5.03.

Semicarbazone. To 0.15 g of 2-acetyl-4-hydroxy-5-carbomethoxy-coumaran in 20 ml of methanol, 0.1 g (about 2 moles) of semicarbazide hydrochloride was added, together with 0.1 g of sodium acetate. After heating for many hours on a water bath with subsequent cooling, the semicarbazone separated. Colorless needles, m.p. 246.5-247°. Yield 0.12 g.

0.0932 g substance: 11.13 ml N_2 (25°, 732 mm); 0.0844 g substance: 10.12 ml N_2 (24°, 730 mm). Found %: N 14.23, 14.37. $C_{13}H_{15}O_5N_3$. Calculated %: N 14.33.

2-Acetyl-4-hydroxy-5-carboxy-coumaran. The hydroxycoumaran carboxylic acid was prepared by saponifying its methyl ester. 1 g of ester was heated for 30 minutes on a water bath with 50 ml of sodium hydroxide (2.5 g), to which alcohol was added. The ester rapidly went into solution, which assumed a dark color.

After cooling the reaction flask, water was added to the contents, and the whole filtered off, the filtrate acidified with strong hydrochloric acid, until it reacted acid to Congo-red. The acid which separated was purified by dissolving it in a solution of potassium bicarbonate, the solution was filtered off and acidified with acetic acid. This operation was repeated. The acid was twice recrystallized from dilute acetic acid. Almost colorless crystalline product, with m.p. 236-237° (in a closed capillary). The yield was about 0.7 g. The acid gave a dark blue coloration with an alcoholic solution of ferric chloride.

0.2346 g substance: 0.4913 g CO_2; 0.1021 g H_2O; 0.2541 g substance: 0.5311 g CO_2; 0.1111 g H_2O. Found %: C 57.12, 57.01; H 4.84, 4.86. $C_{10}H_{10}O_5$. Calculated %: C 57.14; H 4.76.

2-Acetyl-4-hydroxy-coumaran (V). The previous compound was decarboxylated by the quinoline method. 5 g of acid were heated with 150 g of quinoline, dried over barium oxide, and 25 g of bronze on an oil bath for an hour at the b.p. of quinoline. After cooling and adding ether, the solution was filtered from the bronze and was washed with dilute hydrochloric acid. The hydrochloric extract was treated with ether, the ethereal extracts united, dried with magnesium perchlorate and the solvent distilled off. The dark brown residue was thrice recrystallized from water, to which activated carbon was added; almost colorless prismatic crystals were obtained with m.p. 184-185°. Yield 3.65 g. No coloration with ferric chloride.

0.2222 g substance: 0.5566 g CO_2; 0.1137 g H_2O; 0.1884 g substance: 0.4397 g CO_2; 0.0971 g H_2O. Found %: C 67.27, 67.23; H 5.69, 5.73. $C_{10}H_{10}O_3$. Calculated %: C 67.41; H 5.62.

Benzoate of the preceding compound. 0.2 g of coumaran, 3.5 g of benzoic anhydride, and 0.3 g of heat-dried sodium benzoate were heated at 180-190° on an oil bath for 6 hours. The reaction mixture was then poured into water, and extracted with ether. The ethereal extracts were united and treated with 5% NaOH, washed with water and dried over sodium sulfate. After evaporating off the solvent, the residue was crystallized twice from aqueous methanol. Colorless silky needles, melting at 118-118.5°.

0.0938 g substance: 0.2486 g CO_2; 0.0421 g H_2O; 0.2448 g substance: 0.6487 g CO_2; 0.1110 g H_2O. Found %: C 72.30, 72.28; H 4.99, 5.04. $C_{17}H_{14}O_4$. Calculated %: C 72.34; H 4.96.

Oxime. 0.25 g of 2-acetyl-4-hydroxycoumaran was taken for oximation, together with 0.75 g of hydroxylamine hydrochloride, 0.8 g of barium carbonate, and 20 ml of 1:1 alcohol. The mixture was heated together for 1 hour on a water bath under reflux. The hot solution was filtered, and after cooling, the oxime crystallized out as platelets, m.p. 224-225°, yield 0.18 g.

0.1123 g substance: 7.72 ml N_2 (24°, 724 mm); 0.1263 g substance: 7.81 ml N_2 (25°, 726 mm). Found %: N 7.31; 7.23. $C_{10}H_{11}O_3N$. Calculated %: N 7.25.

4-Hydroxycoumaranyl-dimethylcarbinol (VI). 5.2 g of 2-methyl-4-hydroxycoumaran was dissolved, by heating, in 120 ml of absolute benzene free from thiophene, to which 30 ml of dry anisole had been added, to impede the crystallization of the hydroxycoumaran on cooling. The Grignard reagent was prepared, in the usual way, from 4.55 g of methyl iodide and 1.56 g of magnesium, this being in the ratio of 1.1 mole to 1 mole of hydroxycoumaran, with 15 ml of dry ether. The ethereal solution of the methyl magnesium iodide was diluted with 25 ml of benzene and 20 ml of anisole, all well mixed together mechanically; with a slow stream of nitrogen passing through the mixture, a warm solution of hydroxycoumaran (40°) was poured into it over the course of about 20 minutes. After a certain time a voluminous deposit commenced to form. After the ether had been sucked off under a small vacuum (by a slight reduction of pressure) the heating was continued for 2 hours under reflux. At this time the reaction was assumed to be at an end. The reaction product was decomposed with ice and 30% sulfuric acid. A benzene extract was made from the aqueous solution; this was united with the main portion and dried over magnesium perchlorate. After the solvent had been distilled off in vacuum, the residue was collected in the form of a greasy mass and recrystallized from aqueous methanol: the colorless product had an m.p. of 44-46°. The yield of coumaran-carbinol was 3.3 g.

0.1346 g substance: 0.3266 g CO_2; 0.0873 g H_2O; 0.1274 g substance: 0.3091 g CO_2; 0.0833 g H_2O. Found %: C 66.18, 66.17; H 7.23, 7.25. $C_{10}H_{18}O_3$. Calculated %: C 66.29; H 7.18.

Preparation of the carbinol bromide (VII). The coumaranyl-carbinol for this preparation of the corresponding bromide, was saturated in ethereal solution with dry hydrogen bromide gas. At the end of the reaction the reaction mass had assumed a dark brown color. On distilling off the solvent a non-crystallizing oil was obtained, which was not capable of distillation even in vacuum, because of the liberation of HBr from it. To identify the bromide it was decided to obtain its acetate by acting on it with silver acetate but, instead of the expected ester, we obtained tubanol in satisfactory yield.

Preparation of tubanol from the bromide by the action of silver acetate. 4.4 g (1 mole) of the brominated derivative and 6.44 g (2 mole) of silver acetate, with 200 ml of dry benzene were heated under reflux for 2½ hours. The mixture was filtered from the solid product while still hot, the filtrate was evaporated to 30 ml, cooled with ice and the mixture set aside to crystallize for 2 days. No crystalline product separated. The solvent was then distilled off in vacuum, and the residue itself distilled in vacuum. 2.1 g of tubanol was collected (instead of the 4 g expected theoretically), in the form of a colorless oil with a b.p. of 150-151° (9 mm) $[\alpha]_D^{\pm}0°$.

Tubanol gives a clear indication of unsaturation with potassium permanganate. No coloration was given with ferric chloride, as was to be expected.

0.1123 g substance: 0.3080 g CO_2; 0.0700 g H_2O; 0.0958 g substance: 0.2628 g CO_2; 0.0594 g H_2O. Found %: C 74.81, 74.83; H 6.93, 6.90. $C_{11}H_{12}O_2$. Calculated %: C 75.00; H 6.81.

Preparation of tubanol by action of alcoholic alkalies. To 4.6 g of the bromide in absolute alcohol double the theoretical quantity of alcoholic KOH (0.9 g) was added. The total volume of alcohol was 70 ml. The mixture was boiled on a water bath for 4 hours. The excess alcohol was distilled off under a slight vacuum, the residue taken up with ethyl acetate, dried with magnesium perchlorate, and after the solvent had been driven off the tubanol was distilled in vacuum. B.p. 156-157° 10 mm, Yield 2.4 g.

Carboxylation of tubanol and tubaic acid. 5 ml of absolute methanol, 0.3 g of metallic sodium, 0.4 g of tubanol and about 5 g of solid carbon dioxide were placed in a steel capsule of 50 ml capacity. The plug of the capsule was screwed on, and the capsule itself heated in an oil bath for 2 hours at 150-160°. After cooling, the contents of the capsule were poured out into 30 ml of distilled water, and the solution then carefully acidified with hydrochloric acid. The mixture was treated with four 25 ml portion of ether, and the united extracts were dried with sodium sulfate. After distilling off the solvent the pasty residue was dissolved in toluene (23 ml), using activated carbon, the solution was filtered and cooled with a cooling mixture. Colorless small needles which, after repeated crystallization from the same solvent, melted sharply at 126.5-127°. The yield of tubaic acid was 0.38 g $[\alpha]_D^{\pm}0°$. Takei and Koide [11], give 129° for the m.p. of the optically active form, obtained by cleavage of natural rotenone. The preparation which we synthesized gave an intense coloration with ferric chloride, characteristic of o-phenolic acids.

0.1344 g substance: 0.3219 g CO_2; 0.0676 g H_2O; 0.1226 g substance: 0.2935 g CO_2; 0.0604 g H_2O. Found %: C 65.34, 65.29; H 5.59, 5.48. $C_{12}H_{12}O_4$. Calculated %: C 65.46; H 5.45.

Oxidation of tubaic acid with potassium permanganate. A 4% aqueous solution of $KMnO_4$ (55 ml) was added, with vigorous stirring to a suspension of tubaic acid (0.5 g) in acetone (15 ml), over 4 hours; 3 ml of sulfuric acid was also added. Towards the end of the reaction a weak stream of sulfur dioxide was passed through the mixture, which was heated for a short time on the water bath. The presence of acetic acid in the oxidation products was proved qualitatively by the specific lanthanic reaction - a slimy precipitate of basic lanthanum acetate, giving a blue color when iodine was added to it.

Cesium salt of tubaic acid. 1 g of cesium carbonate in 25 ml of distilled water was added to 0.4 g of the acid, the mixture was heated, and the solution filtered while still hot. On cooling, beautiful red crystals separated which, after drying, collectively weighed 0.68 g. M.p. about 215°.

0.2444 g substance: 0.4890 g Cs_2PtCl_6. Found %: Cs 37.83. $C_{11}H_{11}O_2COOCs$. Calculated %: Cs 37.76.

The isomerization of tubaic acid into isotubaic acid: The isomerization of synthetic tubaic acid into isotubaic acid was made according to the method reported by Haller [8]. We took Butenandt's remarks into account [9]. From a 1.3 g sample, 0.7 g of isotubaic acid, m.p. 182° (from toluene), was obtained. The acetate had an m.p. of 150°. Comparison with data in the literature gave figures of 183° and 153° respectively. The isotubaic acid which we synthesized, following the directions of Shriner and Witte [10], although in smaller yield than that claimed by these authors, gave no depression of the melting point when mixed with the pure preparation, obtained by the isomerization of tubaic acid.

SUMMARY

1. Tubanol and tubaic acids, important fragments of the molecule of rotenone, the insect and fish poison, have been synthesized for the first time.

2. The synthesis started from 2-acetyl-4-hydroxy-5-carbomethoxycoumarone, and involved hydrogenation on palladized carbon; only the furan ring was hydrogenated, the carbonyl group not being attacked under these conditions. 2-Acetyl-4-hydroxy-5-carbomethoxycoumaran was obtained.

3. The next stage of the synthesis involved the saponification and decarboxylation of the preceding compound with the formation of 2-acetyl-4-hydroxycoumaran, which was converted to the tertiary alcohol 4-hydroxycoumaranyldimethylcarbinol in a Grignard reaction. Bromination and elimination of the

elements of hydrogen bromide with silver acetate or alcoholic alkali produced tubanol. The tubanol was converted to tubaic acid by Kolbovsky's method.

4. Tubaic acid was identified by converting it to the known isotubaic acid, and by other data.

5. The Japanese investigators Takei and Koide, when describing the establishment of the structure of tubanol and of tubaic acid (which they did approximately) stated in 1929 that in their formulas " the position of the substituents remains, however, unverified". With our synthesis the problem of their structure disappears.

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THE STRUCTURE OF LEDOL

II. HYDRO-DERIVATIVES OF LEDOL, LEDENE, AND LEDDIENE

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In a previous communication [1] it was shown that when ledol is acted on by certain acids, at least two types of hydrocarbon may be formed, differing sharply from one another in structure. Thus, on heating ledol with 90% formic acid, leddiene is formed, which is a bicyclic hydrocarbon of formula $C_{15}H_{24}$, with two double bonds. The experiments described below, relating to the hydrogenation of ledene and leddiene, provide additional confirmation of the formation of different hydrocarbons from ledol. Upon hydrogenation, ledene is mainly converted to dihydroledene, while hydrogenation of leddiene under the same conditions produces di- and tetra-hydroleddienes. These hydro-derivatives of ledene and leddiene approximated a hydrocarbon of the azulene series of the same composition, but of different origin, as is evident from a comparison of their properties (Table). Apart from this, there are three substantial results of the present work, which are important for the chemistry of ledol and of its derivatives, and which may have, perhaps, a more general interest. Dihydroledene, referred to in this paper, remains practically unchanged when acted upon by acids, in contrast to ledene, although, it possesses the cyclopropane ring like the latter, (judging by exaltation). This demonstrates that the cyclopropane ring in ledene is opened by some means, owing to the presence of the double bond.

It is interesting that ledol, which appears to be saturated, may be hydrogenated. This may be explained, apparently, by the fact that ledol, having a mobile hydroxyl group, may easily detach water under the conditions of hydrogenation, and the resulting double bond is hydrogenated. The dihydroledene thus obtained differs in properties from the compounds prepared by Komppa [3]. Finally, it seems that the method recommended by certain authors for the qualitative detection of substances with the azulene skeleton [2]. (bromine in chloroform or acetic acid), is ineffective where the compound belongs to the saturated series. Dehydrogenation appears to be the sole method by which the presence of the azulene group can be detected in saturated substances.

EXPERIMENTAL

Hydrogenation of Ledol. Preparation of dihydroledene. 5 g of ledol with 7 ml of glacial acetic acid were hydrogenated in the presence of 0.2 g of platinum black. In the course of 7 hours 542 ml of hydrogen were absorbed. The mixture in the reaction vessel separated into two layers. The upper layer was decanted, washed with water and caustic soda, and steam distilled. A colorless oil was obtained, which after distillation from Na had the characteristics:

B.p. 102-105° (3 mm); d_{20}^{20} 0.9023; n_D^{20} 1.4840; α_D^{19} -13.92°. MRD 65.33; Calc. 64.87.

Found %: C 87.44, 87.26; H 12.64, 12.61. $C_{15}H_{26}$. Calculated %: C 87.38; H 12.62.

The hydrocarbon obtained is levorotatory dihydroledene, it does not react with bromine in chloroform or acetic acid, nor does it decolorize permanganate in acetone.

Hydrogenation of Ledene. Preparation of dihydroledene. For this preparation a sample of ledene was taken, having d_{20}^{20} 0.9312 and n_D^{20} 1.5006. 0.88 g of platinous oxide was reduced in 10 ml of acetic acid (165 ml of hydrogen were absorbed). 5 g of ledene were added to the Pt black. The hydrogenation took three hours. In all, 612 ml of H_2 were consumed (21°, 761 mm). 549 ml of H_2 (at 0° and 760 mm) are required for the one double bond. The mixture was neutralized with caustic soda, the oil steam distilled, dried with anhydrous Na_2SO_4, and redistilled from sodium:

B.p. 103-106° (3-4 mm); d_{20}^{20} 0.9033; n_D^{20} 1.4839; α_D^{18} +2.87°; MR_D 65.23; Calc. 64.87.

Found %: C 87.05, 87.16; H 12.67, 12.70. $C_{15}H_{28}$. Calculated %: C 87.38; H 12.62.

Name of Hydrocarbon	Origin	Composition	d_{20}^{20}	n_D^{20}	α_D	MR_D Found	MR_D Calc.
Dihydroledene	From ledol	$C_{15}H_{28}$	0.9033	1.4839	+ 2.87°	65.23	64.87
Dihydropalustrene	From palustrol	$C_{15}H_{28}$	0.9036	1.4852	+ 5.44°	65.36	
Tetrahydroleddiene	From ledol	$C_{15}H_{28}$	0.8816	1.4765	+ 3.18°	66.69	>67.07
Tetrahydropalustradiene	From palustrol	$C_{15}H_{28}$	0.8803	1.4773	+ 3.2°	66.79	
Tetrahydroshairene	From shairol	$H_{15}H_{28}$	0.8835	1.4788	+ 26.67°	66.74	
Dihydroleddiene	From ledol	$C_{15}H_{28}$	0.8893	1.4858	+ 1.92°	66.48	66.6
Dihydropalustradiene	From palustrol	$C_{15}H_{28}$	0.8855	1.4834	+ 5.12°	66.49	

It is remarkable that ledene, on hydrogenation, gives dextrorotatory dihydroledene, in contrast to the dihydroledene obtained by the direct hydrogenation of ledol.

The dihydroledene prepared did not give any coloration with bromine in chloroform or acetic acid, but only a weak-violet-blue color on the following day. However, on dehydrogenating dihydroledene with selenium, a violet liquid forms quite easily.

Hydrogenation of Leddiene: a) Preparation of tetrahydroleddiene. 1.71 g of leddiene (d_{20}^{20} 0.9039; n_D^{20} 1.4991), 5 ml of glacial acetic acid, and 0.1 g of Pt black were used. In the course of 8 hours, 352 ml of H_2 were consumed, of which 180 ml were absorbed in the first 30 minutes, after which the hydrogenation slowed down very considerably. The solution was neutralized with soda and steam distilled. A colorless oil was obtained.

B.p. (over Na) 97-100° (3 mm); n_{20}^{20} 0.8816; n_D^{20} 1.4765; α_D^{18} + 3.18°. MR_D 66.69; Calc. 67.07.

Found %: C 86.53; H 13.48. $C_{15}H_{28}$. Calculated %: C 86.53; H 13.46.

Tetrahydroleddiene does not react with bromine and does not decolorize $KMnO_4$ in acetone solution.

b) Preparation of dihydroleddiene. The leddiene used had the following physical constants: d_{20}^{20} 0.9036, n_D^{20} 1.4994. 0.15 g of platinous oxide was reduced in 10 ml of glacial acetic acid, and afterwards 2 g of leddiene was added to the mixture. In 25 minutes 288 ml of H_2 were absorbed (20°, 758 mm), which is close to that required for one double bond (219 ml, 0°, 760 mm). The solution was neutralized with caustic soda, the oil was steam distilled, and afterwards redistilled from sodium.

B.p. 100-103° (3-4 mm); d_4^{20} 0.8893; n_D^{20} 1.4853; α_D^{18} + 1.92°. MR_D 66.48; Calc. 66.603.

Found %: C 87.25; H 12.79. $C_{15}H_{28}$. Calculated %: C 87.37; H 12.62.

The dihydroleddiene easily gives a violet coloration with bromine in acetic acid or chloroform. It easily decolorizes permanganate in acetone solution.

Action of 90% HCOOH and ethylsulfuric acid upon dihydroledene. a) 2 g of dihydroledene (d_4^{20} 0.9033; n_D^{20} 1.4842) were heated just to the boiling point with 4 ml of 90% formic acid for 30 minutes. The mixture was neutralized with soda and steam distilled. 2.2 ml of a colorless oil was obtained.

n_D^{20} 1.4853; d_4^{20} 0.9020; α_D^{18}-12.16° (in 2.5 cm tube α_D^{18}-3.04°). MR_D 65.48. $C_{15}H_{28}$. Calc. MR_D 66.603. $C_{15}H_{28}$. Calc. MR_D 64.87.

Thus dihydroledene is scarcely changed by heating it with formic acid (distinction from ledene, which is easily converted to leddiene under these conditions).

b) 2 g of dihydroledene (d_4^{20} 0.9033; n_D^{20} 1.4842) was dissolved in 8 ml of ethyl alcohol, containing 0.4 ml of sulfuric acid (d. 1.84). After heating on a water bath for 30 minutes the solution was diluted with water, the oil extracted, washed with water, and steam distilled. A colorless oil was obtained, d_4^{20} 0.9033; n_D^{20} 1.4879; MR_D 65.69. Repeated heating of dihydroledene under these conditions produced small changes in its phydical constants.

SUMMARY

1. Ledol and ledene yield dihydroledene on hydrogenation, a hydrocarbon of composition $C_{15}H_{28}$. In contrast to ledene, dihydroledene is quite stable to acid reagents.

2. Leddiene yields two derivatives: a di- and a tetraderivative on hydrogenation ($C_{15}H_{28}$ and $C_{15}H_{28}$).

3. The results confirm that by dehydrogenation under definite conditions, ledol can yield either ledene, a tricyclic hydrocarbon of composition $C_{15}H_{24}$ with one double bond, or leddiene, a bicyclic hydrocarbon of composition $C_{15}H_{24}$ with two double bonds.

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THE STRUCTURE OF LEDOL

III. THE HYDROCARBON SKELETON OF LEDDIENE. CRYSTALLINE PRODUCTS OF THE OXIDATION OF LEDENE

N. P. Kiryalov

The factual material available from the study of the sesquiterpene alcohol ledol, whose empirical composition is $C_{15}H_{23}O$, has shown that it is a saturated tertiary tricyclic compound containing the azulene double ring. Only the general plan of the structure of ledol is known, however. Thus the essential details of the structure, such as the character and arrangement of the side chains, the location of the hydroxyl group in the molecule, and the arrangement of the cyclopropane ring remain undecided.

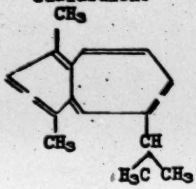
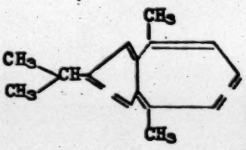
The present paper describes experiments to clarify the character and arrangement of the side chains in ledol, and to find an experimental method for determining the location of the hydroxyl group and of the cyclopropane ring. The character and arrangement of the side chains in ledol was clarified by a comparatively simple method. Ledol (m.p. 105-106°) was dehydrated by boiling with 90% formic acid, and the hydrocarbon formed, which is leddiene of composition $C_{15}H_{24}$, was dehydrogenated with selenium. An azulene was extracted from the blue-violet liquid resulting from the dehydrogenation, and this was used to prepare crystalline derivatives (picrate, styphnate, trinitrobenzolate and trotylate). By comparing the derivatives obtained with derivatives of azulene, $C_{15}H_{18}$ of known structure, it was found that the m.p.'s of the azulene derivatives from leddiene are in agreement with those of guaiazulene derivatives, given in the literature[1] (Table).

Such agreement between the m.p.'s of derivatives suggests that in all probability the carbon skeleton of leddiene is analogous to the carbon skeleton of guaiazulene, and the positions of all 15 carbon atoms in the molecule of leddiene and likewise in that of ledol become clear.

To decide the question of the location of the hydroxyl group, and of the cyclopropane ring, in the ledol molecule, it is necessary to convert ledol or ledene to substances in which the essential part of the structure of ledol remains unchanged. After a number of experiments it was established that a crystalline substance was formed by oxidizing leddiene with potassium permanganate in acetone, having the same number of carbon atoms as are contained in the cyclopropane ring. Thus we obtained: a glycol (which we have named ledglycol) of composition $C_{15}H_{28}O_2$ (m.p. 151-152°) in 45-50% yield, sometimes reaching 60%; probably a keto-acid (ledoic acid) of composition $C_{15}H_{24}O_3$ (m.p. 155-156°) in yield of 5% and a liquid substance whose composition has not yet been established. Some of the oxidation products showed that the ledene used for oxidation was a mixture of 2 or 3 isomers, which is quite probable on theoretical grounds, since the dehydration of ledol may proceed in three different directions. Among the oxidation products of ledene, ledoic acid was investigated in more detail. It was found that this acid easily forms esters (methyl, m.p. 94-94.5°, and ethyl, m.p. 94.5-95°). Of more interest was the behavior of ledoic acid to sodium hypobromite and to potassium permanganate in alkaline solution.[2]

[1] Variations in the m.p.'s of the styphnates are apparently due to variations in purity.

[2] In view of the spontaneous action of potassium hypobromite and permanganate on keto-acids of the sesquiterpene series (observed for the first time) the results described below have undoubted interest.

Name of azulene	Melting Point				Author
	Picrate	Styphnate	Trinitro-benzolate	Trotylate[1]	
Guaiazulene 	122-122.5°	105-106°[2]	151-151.5°	89°	Pfau and Plattner [4]
	122	-	-	89	Radcliffe and Short [6]
	122-121	-	150-151	88-89	Haagen-Smit and Fong[2]
	121-122	105-106[2]	-	-	Ruzicka and Haagen-Smit[7]
Vetivazulene 	121.0-122	-	149-150	80.5-81	Pfau and Plattner [4]
	122	-	151.5	79	Pfau and Plattner [5]
	122.5	95-96.7	154-155	76.5-79.5	Sorensen and Hougen[8]
Azulene from leddiene	121-122	108-109[2]	150-151	89.5-90	Kiryalov [1]

By oxidation with sodium hypobromate under comparatively mild conditions, ledoic acid forms an hydroxy acid of composition $C_{15}H_{24}O_4$ (m.p. 144.2-144.8°) in good yield. We named this α-hydroxyledoic acid. Preparation of a number of derivatives of this acid (the ethyl ester, acetyl derivatives etc), disposed of any doubt that the oxygen which enters the molecule of ledoic acid during oxidation with sodium hypobromite, is fixed as a hydroxyl group. This fact establishes that the carbonyl group, which is present in ledoic acid, is probably quite resistant to the action of hypobromite, and in any case is more stable than other parts of the molecule. Besides α-hydroxyledoic acid, the oxidation of ledoic acid with hypobromite gives carbon tetrabromide (m.p. 92°) and a colorless acid liquid in small quantity (20-25% of the weight of ledoic acid). On account of the uncertainty of the results, the liquid part was not studied further. However, it is possible that the liquid acid part of the oxidation products is a dibasic acid of different composition, i.e. ledoic acid may be oxidized with hypobromite in the same way as has been shown in the literature for compounds containing the CH_3CO group [3]. By the action of potassium permanganate in alkaline solution a β-hydroxyledoic acid of composition $C_{15}H_{24}O_4$ (m.p. 178-179.3°), is obtained in theoretical yield. The oxidation products of ledene (ledglycol and ledoic acid) and a number of derivatives of ledoic acid are well crystallized substances with sharp melting points, thanks to which they may be used for the identification of ledol and ledene. Crystalline

[1] "Trotyl" is a pseudonym for T.N.T.[1]

[2] Differences in the m.p.'s of the styphnates are apparently due to differences in purity.[2]

derivatives of ledene have not been known until now, and this has made the investigation of its nature difficult. Ledglycol and ledoic acid are substances of undoubted interest for clarifying details of the structure of ledol.

EXPERIMENTAL

Dehydrogenation of leddiene and preparation of azulene derivatives. 20 g leddiene (prepared by dehydration of ledol with 90% formic acid; d_{20}^{20} 0.9040; n_D^{20} 1.4993) was heated to boiling with 10 g of selenium for 6-7 hours. The product was extracted with benzene, steam distilled, and extracted with 50% sulfuric acid. The acid solution was poured into cold water (triple quantity), and extracted with ether. The ethereal solution of azulene was purified by steam distillation. After drying and distilling off the ether, azulene was obtained.

Picrate. A hot saturated alcoholic solution of picric acid (2 g) was added to 2 g of azulene in 3 ml of ethyl alcohol. Black needles melting at 121-122° (from alcohol) were obtained. The picrate (2 g) was decomposed by steam distillation in the presence of 0.5 g NaOH. The azulene which separated was collected in a graduated cylinder. It was violet-blue in color. Yield 0.9 ml (about 45%).

Styphnate. 0.3 g azulene (purified via the picrate) was mixed with 0.3 g of trinitroresorcin in 1 ml of alcohol. Dark colored needles with m.p. 108-109° (from alcohol after 4-5 recrystallizations). The styphnate dissolves better in alcohol than the picrate.

Trinitrobenzene derivate. 0.3 g azulene (purified via the picrate) in the minimum quantity of alcohol was mixed with a saturated alcoholic solution of trinitrobenzene (0.3 g). Dark colored needles of the trinitrobenzene derivative were precipitated; these are very soluble in alcohol, in which they give a blue coloration. Yield 0.5 g, m.p. 150-151°.

Trotylate. 0.3 g azulene in the minimum quantity of alcohol was mixed with a saturated alcoholic solution of 2,4,6-trinitrotoluene (0.5 g). Black needles of trotylate were formed immediately. These are very soluble in alcohol, and melt at 89.5-90°. The compound dissolves in alcohol with a blue coloration.

Oxidation of ledene with potassium permanganate in acetone. Ledene was obtained by dehydration of ledol (m.p. 105-106°) with ethylsulfuric acid, by heating to the boil for 4-5 minutes. The method has been described in detail previously [1]. 24 g of ledene (d_{20}^{20} 0.9260-0.9312; n_D^{20} 1.500-1.5013) were dissolved in 700 ml of acetone, and a 10% aqueous solution of $KMnO_4$ (350 ml) was added to it, the mixture being gradually cooled with water at the same time. After the permanganate had been decolorized, the solution was filtered (the manganese dioxide was washed with acetone and water); the acetone was distilled off and the residual liquid containing oily droplets was cooled. The crystals which separated were filtered and recrystallized from gasoline or aqueous alcohol. M.p. 151-152° (needles from gasoline; platelets from alcohol). The yield of pure substance was 11.5 g (sometimes up to 60% on the weight of ledene). The alkaline filtrate was evaporated to small volume and acidified; a small quantity (1-2% on the weight of ledene) of a crystalline substance was obtained, m.p. 155-156° (from aqueous alcohol). Oxidation of ledene with an acetone solution of permanganate alone, lowered the yield of substance of m.p. 151-152° to 10%, but the yield of substance m.p. 155-156° was increased to 5%. Among the oxidation products a thick oily liquid was found which, on standing, liberated a small quantity of substance of m.p. 151-152°.

Investigation of the substance melting at 151-152°. This substance dissolved well in acetone, alcohol, ether, chloroform, and hot gasoline; it dissolved poorly in cold gasoline and was insoluble in water:

α_D^{21} −0.92° (in 5% alcoholic solution); $[\alpha]_D^{21}$ −18.4°.

Found %: C 75.32, 75.45; H 11.12, 11.03. $C_{15}H_{26}O_2$. Calculated %: C 75.63; H 10.92. 0.0922 g substance: 16.5 ml CH_4 (0°, 760 mm). The substance was previously dissolved in warm xylene (to 50°). $C_{15}H_{24}(OH)_2$. Calculated: 17.35 ml CH_4.

Analysis show that the substance is a glycol. Ledglycol does not react with bromine in chloroform solution. On heating with selenium, a liquid of violet color was formed. The ledglycol was not affected by boiling with alcoholic alkali.

Investigation of the substance melting at 155-156° (ledoic acid). This dissolves in ether, alcohol, acetone and alkalies; it dissolves poorly in hot water and not at all in cold water.

α_D^{21} + 15.8° (in 12.5% alcoholic solution); $[\alpha]_D^{21}$ + 126.4°. Found %: C 71.50, 71.57; H 9.56, 9.49. $C_{15}H_{24}O_3$. Calculated %: C 71.43; H 9.52. 0.0538, 0.0547 g substance: 2.1, 2.15 ml 0.1 N NaOH. $C_{14}H_{23}O(COOH)$. Calculated: 2.13, 2.17 ml 0.1 N KaOH.

The silver salt was obtained by the action of $AgNO_3$ on the aqueous solution of the neutralized sodium salt of ledoic acid. Pale yellow precipitate. On drying in vacuum it turned gray.

Found %: Ag 30.2. $C_{15}H_{23}O_3Ag$. Calculated %: Ag 29.88.

Preparation of the ethyl ester of ledoic acid. 0.5 g of the acid was dissolved in 10 ml of 95% ethyl alcohol, containing 0.4 ml of sulfuric acid (d. 1.84). The solution was heated on a water bath for 30 minutes. After cooling 50 ml of water were added; the ester was filtered off and recrystallized from aqueous alcohol; colorless needles of m.p. 94.5-95°. The yield was quantitative. The substance dissolved well in acetone, ether, alcohol and was insoluble in water.

Found %: C 72.76, 72.72; H 10.02, 10.08. $C_{17}H_{28}O_3$. Calculated %: C 72.85; H 10.00.

The ethyl ester does not contain the hydroxyl group (negative Tserevitinov reaction). Saponification of the ester yielded the original ledoic acid.

The methyl ester of ledoic acid was obtained by boiling the acid with methyl alcohol plus sulfuric acid, under conditions similar to those for the preparation of the ethyl ester. The yield was quantitative. Needles, m.p. 94-94.5°. Admixture of the ethyl ester depressed the m.p. very little (m.p. of mixture 93-93.8°).

Found %: C 71.84, 71.77; H 9.89, 9.73. $C_{16}H_{26}O_3$. Calculated %: C 72.18; H 9.77. 0.095 g substance: 8.8 ml CH_4 (0°, 760 mm) in xylene. $C_{16}H_{25}O_2(OH)$. Calculated: 8.4 ml CH_4.

By saponifying the methyl ester with one equivalent of alkali the original acid was obtained (no depression in mixed m.p. with ledoic acid).

Behavior of ledoic acid with semicarbazide. 0.3 g of acid was mixed with 0.3 g of semicarbazide hydrochloride and 0.3 g of sodium acetate. The mixture was heated on a water bath in aqueous alcohol for 7 days. The yield of crystalline precipitate was very small; m.p. 246-248° (with decomposition and volatization of the substance). The substance scarcely dissolved in ether, alcohol or water.

Oxidation of ledoic acid with alkaline bromine. 1 g of ledoic acid was neutralized with aqueous caustic soda so that, after neutralization, the volume of liquid was not greater than 50 ml. To the solution of the salt of the acid obtained, a mixture of 15 ml of aqueous caustic soda (10%) and 2.2 g bromine was added. The mixture was heated to 50° for 20 minutes, and afterwards stood for 18 hours at room temperature. The mixture gradually lost its color, and a crystalline precipitate collected on the bottom of the flask. Afterwards the liquid was heated to 50° for a further 3 hours and was then filtered off; it was nearly colorless. The crystalline product melted at 92° (from aqueous alcohol) and gave no depression on melting in admixture with carbon tetrebromide. The yield was 0.2 g. The filtrate was cooled in ice water, treated with 3 ml of concentrated sodium sulfite, and afterwards acidified with dilute sulfuric acid. The copious precipitate obtained was filtered off and recrystallized from aqueous alcohol or isoamyl acetate. M.p. 144.2-144.8° (after 3-4 recrystallizations). The substance crystallizes in fine needles, which dissolve well in ether, alcohol, hot water and alkalies. The yield was 0.7-0.8 g. Repeated oxidation under the conditions indicated, always produced the same substance. From the acid filtrate, saturated with sodium chloride, a thick acid liquid was extracted by ether, in quantity 20-25% of the weight of the ledoic acid. The liquid dissolved well in water but was not further investigated.

Investigation of the substance melting at 144.2-144.8° (hydroxy-ledoic acid).

Found %: C 66.88; H 9.07. $C_{15}H_{24}O_4$. Calculated %: C 67.16; H 8.95.

To determine the quantity of hydroxyl group the mixture was heated to 50°. At room temperature, a yellowish precipitate was formed, which made the reaction more sluggish, and the results of the determination were lowered by 15-25%. 0.1095 g substance: 17.1 ml CH_4 (0°, 760 mm). $C_{15}H_{22}O_2(OH)_2$. Calculated: 18.2 ml CH_4. 0.0958, 0.0636 g substance: 3.55, 2.33 ml 0.1 N NaOH. $C_{14}H_{23}O_2COOH$. Calculated: 3.57, 2.37 ml 0.1 N NaOH.

The silver salt was obtained by mixing concentrated aqueous solutions of equivalent quantities of the sodium salt and $AgNO_3$; the salt precipitated as a yellow substance which dissolved well in water and alcohol. The salt was filtered off, washed with ice water, dried in vacuum (in the dark). The substance darkens on drying.

Found %: Ag 29.6. $C_{14}H_{20}O_2COOAg$. Calculated %: Ag 28.8.

Preparation of the ethyl ester. 10 ml of absolute (or 96%) alcohol, containing 0.5 ml sulfuric acid, were heated to boiling for 10 minutes with 1 g of the acid under examination. After cooling, the mixture was diluted with water, and extracted with ether; the ethereal solution was washed with caustic soda and water, dried with anhydrous Na_2SO_4, and the ether distilled off. The substance obtained had an m.p. of 78-79°; after recrystallization from aqueous alcohol it melted at 79-80° (needles).

Found %: C 68.73; H 9.60. $C_{17}H_{28}O_4$. Calculated %: C 68.92; H 9.39.

Saponification of this ester gave an acid of m.p. 143-144°, which gave no m.p. depression with α-hydroxyledoic acid. One equivalent of alkali was used for the saponification. The ethyl ester of α-hydroxyledoic acid which was obtained contained a hydroxyl group.[1]

0.1414 g substance: 10.3 ml CH_4 (0°, 760 mm) in xylene. $C_{17}H_{27}O_3OH$. Calculated: 10.7 ml CH_4.

1) 25 ml solvent; the reaction vessel was heated to 50°, since in contrary cases a yellowish precipitate was formed and the results of the determination were lowered by approximately 20%.

The presence of the hydroxyl group in α-hydroxyledoic acid was confirmed by preparation of the acetate. 2 g of α-hydroxyledoic acid was heated to boiling with 10 ml of acetic anhydride and 0.2 g of sodium acetate. After 1 hour 20 ml of water were added to the mixture, and the solution evaporated to a small volume. After cooling, long, needle-like crystals separated, with m.p. 165.5-166.8° (from aqueous alcohol). Yield 0.8 g.

Found %: C 65.56; H 8.47. $C_{17}H_{28}O_5$. Calculated %: C 65.80; H 8.39.

In neutralizing 0.1042 g of the acetate of α-hydroxyledoic acid, 3.21 ml of 0.1 N NaOH was used (calc. 3.36 ml of 0.1 N NaOH).

Saponification of 0.1042 g of the neutralized acetate consumed 3.47 ml of 0.1 N NaOH (Calculated 3.36 ml 0.1 N NaOH). The acid obtained melted at about 144°, and gave no m.p. depression with α-hydroxyledoic acid.

Boiling the acetate in ethyl alcohol with 2-3 drops of sulfuric acid gave, very easily, needle-like crystals of m.p. 85.5-86.5°(from aqueous alcohol). The substance appears to be the ethyl ester of acetylated α-hydroxyledoic acid.

Found %: C 66.73; H 9.06. $C_{19}H_{30}O_5$. Calculated %: C 67.45; H 8.93.

The ester has a neutral character. In saponification it consumes 2 equivalents of alkali; acidification yields an acid which gave no depression with α-hydroxyledoic acid. α-Hydroxyledoic acid gave no semicarbazone.

Oxidation of ledoic acid with an alkaline solution of potassium permanganate. 2.2 g of the acid (m.p. 155-156°) was dissolved in 20 ml of water containing 0.6 g KOH, and 100 ml 2.8% potassium permanganate, containing 1 g of caustic potash was added gradually, with continuous agitation and cooling with water. The mixture was kept for 40 hours in a cool place. The solution, decolorized with 2-3 drops of methyl alcohol, was filtered and the manganese dioxide was washed with water. The filtrate was acidified with dilute sulfuric acid (5-10%); the liquid, together with the copious precipitate, was extracted with ether, the ether distilled, and the precipitate recrystallized from aqueous alcohol: needles, m.p. 178-179.3°. The yield of pure substance was 2 g. Attempts to prepare the semicarbazone were not successful.

Found %: C 67.22, 67.11; H 9.22, 9.08. $C_{15}H_{24}O_4$. Calculated %: C 67.16; H 8.95. 0.0685 g substance: 11.1 ml CH_4 (0°, 760 mm) in 25 ml heated xylene. $C_{15}H_{22}O_2(OH)_2$. Calculated: 11.45 ml CH_4. 0.1082 g substance: 3.96 ml 0.1 N NaOH. $C_{14}H_{23}O_2COOH$. Calculated. 4.03 ml 0.1 N NaOH.

The silver salt was obtained under conditions similar to those under which the silver salt of α-hydroxyledoic acid was obtained. It dissolved well in water and alcohol.

Found %: Ag 29.72. $C_{15}H_{23}O_3Ag$. Calculated %: Ag 28.8.

The substance which separated was isomeric with hydroxyledoic acid and may be called β-hydroxyledoic acid; it contained one carboxyl group.

Ethyl ester of β-hydroxyledoic acid. 0.5 g of the acid was heated for 30 minutes with 10 ml of absolute alcohol in the presence of 4-5 drops of concentrated sulfuric acid. On cooling, 20 ml of water was added to the solution. A copious precipitate separated almost immediately. The precipitate was filtered and recrystallized from aqueous alcohol. Needles, with an m.p. of 86.5-87.5°. The ester had a neutral reaction; yield about 0.5 g.

Found %: C 68.73; H 9.75. $C_{17}H_{28}O_4$. Calculated %: C 68.91; H 9.46. 0.0988 g of ester was boiled for 45 minutes with 10 ml of an 0.1 N alcoholic KOH; 3.88 ml of 0.1 N KOH were consumed in saponfication: $C_{27}H_{28}O_4$. Calculated: 3.7 ml 0.1 N KOH.

The neutralized saponification product was evaporated to dryness, dissolved in water, acidified with dilute sulfuric acid and extracted with ether. The substance which separated had an m.p. of about 177°, and did not give a depression with the original acid. The ethyl ester (m.p. 86.5-87.5°) contained one hydroxyl group, as is evident from the following determination (in cold xylene).

0.1012 g substance: 5.9 ml CH_4 (0°, 760 mm). $C_{17}H_{26}O_4$. Calculated: 7.66 ml CH_4.

SUMMARY

1. In the dehydrogenation of leddiene with selenium, an azulene of composition $C_{15}H_{18}$ is formed. The following derivatives of this azulene were obtained: the picrate, m.p. 121-122°; the styphnate, m.p. 108-109°; 1,3,5-trinitrobenzene derivative of m.p. 150-151°; the 2,4,6-trotylate, m.p. 89.5-90°. The m.p.'s of the products obtained did not differ from those reported for guaiazulene, from which we conclude that the carbon skeleton of leddiene is structurally analogous to that of guaiazulene.

2. By oxidizing ledene with potassium permanganate in aqueous acetone, there were obtained: ledglycol of composition $C_{15}H_{28}O_2$ with m.p. of 151-152° (yield about 50%) and an acid (ledoic acid) of composition $C_{15}H_{24}O_3$, with m.p. 155-156° (yield about 5%), related, apparently, to keto-acids.

3. Ledoic acid, by mild oxidation with sodium hypobromite, is easily converted to α-hydroxyledoic acid of composition $C_{15}H_{24}O_4$; m.p. 144.2-144.8°. A number of α-hydroxyledoic acid derivatives were obtained and characterized.

4. Alkaline potassium permanganate converts ledoic acid to β-hydroxyledoic acid, of composition $C_{15}H_{24}O_4$, with an m.p. of 178-179.3°.

5. The formation of ledglycol and ledoic acid by oxidation of ledene seems to be characteristic and may be used for diagnosing the presence of the corresponding hydrocarbons in essential oils, as well as for the identification of ledol (after dehydration).

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THE HYPOTHESIS OF THE QUASICOMPLEX STATE AND RELATED QUESTIONS IN THE THEORY OF ORGANIC REACTIONS[1]

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The extensive investigations of A. N. Nesmeyanov and his school constituted an excellent contribution to our knowledge of the metallo-organic compounds. From the theoretical aspect they led to the original conception of a "quasicomplex" structure of some organic molecules [1]. In its original form this hypothesis postulated that the structure of binary metallo-organic compounds can be expressed neither by the classical structural formulas, nor by the formulas of complex compounds, but requires some intermediate form, in which separate molecules and ions "pre-exist"; the existence of these more or less autonomous structures was supposed to predetermine the direction of decomposition of these compounds during chemical reaction [1].

This proposal has subsequently undergone considerable change. It was admitted that, in the unexcited molecule of chlorovinylmercury chloride and analogous compounds, it is not possible to detect the mesomeric tendency which had been expected. Many of the superpositions and mesomers, postulated earlier, were made tentatively or were withdrawn. According to the new point of view, the quasicomplex state is developed mainly at the moment of reaction, and thus has an electromeric, and not a mesomeric, nature [2].

The principal criterion of a quasicomplex compound is now taken to be the presence of hyper- (or σ)-conjugation in the molecule, corresponding to the scheme , which is a condition for easy decomposition of the compound into the components C=C and X-M.

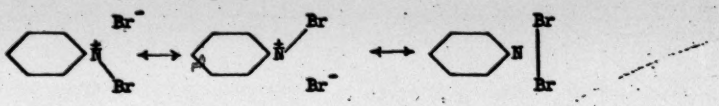
Would it be expedient, however, to classify a substance, said to be quasicomplex, with complex compounds? What is there in common between these two concepts? To this question it is not easy to give a logical answer, because the term "complex compound" has at present no exact limitations, and does not include well-defined premises about the valency state of the bonds [4,5]. The idea of a quasicomplex compound is still more diffuse and indefinite in its systematic and physico-chemical relationships.

If a compound such as $[(NH_3)_3PtCl]Cl$ is taken as a typical complex compound for comparison, then it can easily be established that the hyperconjugation formula does not correspond to the complex structure. According to the principles of coordination theory, compounds such as chlorovinylmercury chloride must be considered as the products of the insertion of acetylene into the molecule of corrosive sublimate, i.e., as $Cl[C_2H_2HgCl]$, the chlorine of the chlorovinyl group should be

[1]) This paper was written in the summer of 1949. While it was in printing new papers by A. N. Nesmeyanov and his co-workers appeared, in which there was a considerable evolution of their hypotheses of the quasicomplex state [2]. On the other hand, in connection with polemics which arose in print [3], the question of the quasicomplex hypothesis overflowed into the general problem of the theory of chemical bonds. Taking this into consideration, and in agreement with the editorial board of the Journal of General Chemistry of the USSR, I introduced fairly considerable changes into my paper, in order to bring the analysis of the quasicomplex hypothesis into line with its current state (January, 1951).

ionogenic (or quasi-ionogenic) while the chlorine in the internal group, that is in the HgCl group, should not be ionogenic. In actual fact matters are quite the contrary. The halogen in the HgCl group is very easily displaced by other anions; the chlorine in the chlorovinyl group shows tendency to be exchanged. Thus the structure $Cl - CH{=}CH - HgCl$ is not subject to coordination principles and can only provisionally be considered as a complex compound [1].

On the contrary, when an attempt is made to extend the quasicomplex concept to compounds of definite complex type, formulas are obtained which are not in accordance with structural realities. This is shown, for example, by pyridine bromide, for which is (or was) proposed the mesomeric structure [6]:



However, it was shown that the bromine atoms in this compound are not equivalent, and that this compound is, in all probability, N-bromopyridine bromide [7].

Analogous considerations apply to other such compounds, interpreted as quasicomplex [6].

On the other hand, A. N. Nesmeyanov and his co-authors consider as a characteristic of the chemical behavior of quasicomplex compounds, their tendency to break down into their components. This property contradicts present-day definitions of complex structure, which do not contain any indication of instability [4], nor even include stability among the characteristics of the complex structure [5].

Actually, it is easy to establish that there is no direct connection between the stability of a compound and the possibility of assigning to it a complex or quasicomplex form. We know that there are very unstable simple compounds and, on the other hand, complex compounds are often very stable. Quasicomplex sulfuric acid is very stable, (according to Lukin [8]), in comparison with nitrous acid, which cannot be considered as a quasicomplex compound, in spite of its decomposition into its anhydride and water. Thus complex ammonium iodide is more stable than the simple copper iodide, KHF_2 is more stable than simple BiH_3 and its derivatives, and so on. Thus, the criterion of instability is superficial and unreliable, when it is desired to establish with its aid the complex or quasicomplex nature of any compound.

The following considerations contradict the conception of quasicomplex compounds as intermediate between covalent and coordinate ones. It may be asserted that the covalent and complex forms exist separately, behaving like mobile isomers. In particular, compounds with multiple bonds have a tendency to form π-complexes with different electronic acceptors [9]. Similarly, ammonia forms ammonium bromide, just as ethylene adds on Hbr, forming the complex structure; $H_2C{=}CH_2$. The existence of such complexes between unsaturated organic compounds and acceptor inorganic compounds follows particularly from kinetic data. Actually, addition is generally

[1]) It is more analogous to an adduct of bipolar ions, such as $ClN_2C_6H_4CO_2H \rightleftarrows Cl^- + {}^+N_2C_6H_4CO_2^- + H^+$ with the difference, it is true, that in the latter case regular chemical equilibrium is established, and mesomerism is not assumed.

a trimolecular reaction [10]. If we do not wish to assume an improbable three-body collision, then we must assume that, initially, the unsaturated compound forms with the agent an unstable complex, which afterwards reacts with the third partner of the reaction. Occasionally these complexes are stable enough to be isolated. However the π-complex nature has not obtained general recognition[1]). [11]. In other cases they have been detected by physico-chemical means. In particular, it was shown that mercurous nitrate forms two compounds with cyclohexene which have the properties of π-complexes [9a]. It follows from the kinetic data that mercuric chloride and acetylene also form initially some sort of π-complex $C_2H_2 \rightarrow HgCl_2$, isomeric with trans and cis-chlorovinylmercury chloride [12]. It is doubtful, therefore, whether it is possible to ascribe to chlorovinylmercury chloride the structure of the intermediate quasicomplex form, once the actual complex form exists independently.

Apparently, analogies with complex compounds cannot in general lead us to an appreciation of the concept and importance of the term "quasicomplex compound". It is more convenient to consider this simply as a synonym of a compound having the possibility of a σ-conjugational displacement.

In such a case, indeed, the terminology of the quasicomplex hypothesis becomes more or less superfluous but, on the other hand, we shall have to deal with a definite and general principle, leading to the question of the mechanism of fission reactions.

3

A. N. Nesmeyanov considers reactions involving the breakdown of quasicomplex compounds as a collapse of a "federation" into its component parts [2]. In the new development of the hypothesis this collapse is connected with the effect of some reagents, facilitating the appearance of the electromeric effect of conjugation in bonds. This idea introduces into the theory a matter of very considerable moment. Nevertheless the role of the cleavage agent still remains underestimated. In the opinion of Nesmeyanov and his co-authors, "the unusual ease of this family of reactions is to be explained...by an elevation of the polarizability of structures of the type indicated" (the type is that of chlorovinylmercury chloride) [14].

However the "unusualness", in essence, is not that of the ease of the breakdown, but rather that of the reagents under whose influence the breakdown proceeds (e.g. potassium chloride or sodium sulfide in aqueous solution). Energetico-data do not disclose the special instability of typical quasicomplex compounds. As our measurements have shown, the decomposition of cis-chlorovinylmercury chloride liberates 13.5 kcal/mole; in the decomposition of the trans-isomer 9.2 kcal/mole are liberated [15]. The effect is of the same order as that of the breakdown of ethanol to ethylene and water ($Q \approx -11$ kcal). However, when cis-chlorovinylmercury chloride is decomposed by a solution of sodium sulfide, 43 kcal/mole are liberated, because of the exothermal formation of mercury sulfide and of the complex $HgS \cdot mNa_2S$ from it, according to the equation:

$$HgCl_2 + (m + 1)\ Na_2S = HgS \cdot mNa_2S + 2NaCl.$$

Thus, the thermodynamic condition is created for a vigorous decomposition. The necessary kinetic conditions are, firstly, the ease of formation of coordinate bonds between the $HgCl$ group and the sulfide ion, and second by the development of a donor-acceptor decomposition mechanism, which will be examined below.

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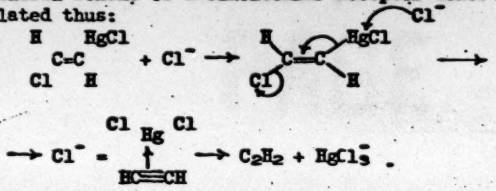
1) It must be observed that the foundations and conclusions of this work do not depend upon assumed forms of π-complex compounds. The fact of their existence alone is of importance.

As has been shown, ethyl alcohol by itself is less stable than cis-chlorovinylmercury chloride. However sodium sulfide cannot react with it, because there is no energetically favorable reaction for this. But, for example, in the presence of an acid, alcohol decomposes at quite low temperatures, while cis-chlorovinylmercury chloride, in the absence of a diluent, and particularly in non-polar solvents, still does not show evidence of decomposition. Moreover it must be assumed that the chlorvinylmercury chlorides can decompose autocatalytically thanks to the fact that they contain the ionogenic HgCl groups in their molecules. It would be useless under these circumstances to compare the "polarizability" of chlorovinylmercury chlorides with that of ethanol or other analogous compounds. Apparently the "polarizability" will always be sufficient for decomposition, if the energetics of the corresponding reaction permits it, both thermodynamically and kinetically.

On the other hand, while it may be observed that chlorovinylmercury chloride reacts more easily with potassium iodide or with hydrochloric acid than do compounds of the type CH_3HgCl, account must be taken of the fact that in the latter case the reaction ought to follow a different path from that followed by chlorovinylmercury chloride. The decomposition cannot have a purely structural cause. Consequently, once again there is no basis for comparing the polarizability of compounds of one type, with those of the other type.

4

In the work of Nesmeyanov and his co-authors, no attempts are made to interpret the mode of action of the reagents which cause the decomposition of quasicomplex compounds. Meanwhile current theory makes it possible to put forward forms of transition complexes for this case, and to give a general picture of the development of chemical processes [14, 16]. We have, for example, sufficient foundation for proposing that the decomposition of trans-chlorovinylmercury chloride follows the general scheme of a bimolecular acceptor-donor mechanism and that it may be formulated thus:



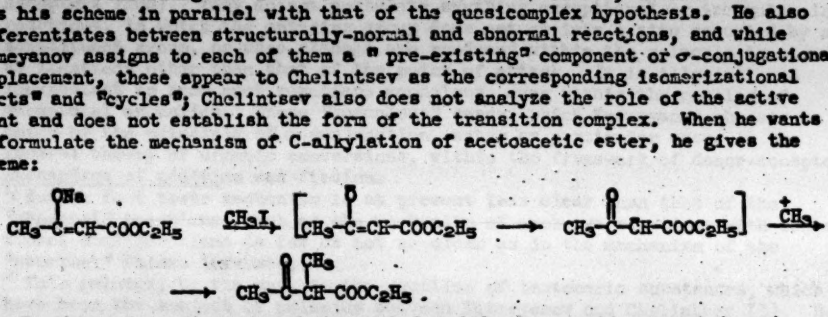
(The bent arrows represent the movement of a pair of electrons at the moment of reaction and are in no way connected with any meso- or electromeric relationships in the molecule).

According to this scheme, the reaction commences when a chlorine ion attaches itself to the Hg atom of the HgCl group, attempting to form $HgCl_2$. At the instant of formation of a new bond, the electron pair between the Hg and C is displaced to the double bond, and the chlorine in the C-Cl group is ionized. The π-complex $C_2H_2 \rightarrow HgCl_2$, is formed as an intermediate compound, which breaks down afterwards, by reaction with a Cl ion, to form acetylene and the complex ion $HgCl_3^-$. The reverse reaction, formation of trans-chlorovinylmercury chloride from $HgCl_2$ and acetylene, proceeds through the same π-complex. The electrons simply move in the opposite direction (arrows in the transition complex are rotated through 180°). From this it follows immediately that the chlorine ion ought to accelerate both the direct and the reverse reactions: this important conclusion escapes the quasicomplex hypothesis, because it examines the state of the unreacted molecule and avoids the examination of the act of reaction itself.[1]

1) See p. 2337.

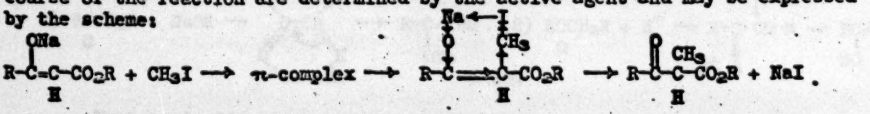
The hypothesis of quasicomplex structure ascribes particular importance to the duplexity (or multiplicity) of the chemical reactions of quasicomplex metalloorganic compounds. Certain of these reactions are reckoned as normal, others as abnormal [2]. "Normal" reactions, apparently, do not require

1) Analogous remarks must be made about the theory of G. V. Chelintsev [17], concerning the mechanisms of organic reactions. In spite of the sharpness of the verdict concerning the ideas of mesomerism and resonance, Chelintsev develops his scheme in parallel with that of the quasicomplex hypothesis. He also differentiates between structurally-normal and abnormal reactions, and while Nesmeyanov assigns to each of them a "pre-existing" component or σ-conjugational displacement, these appear to Chelintsev as the corresponding isomerizational "acts" and "cycles"; Chelintsev also does not analyze the role of the active agent and does not establish the form of the transition complex. When he wants to formulate the mechanism of C-alkylation of acetoacetic ester, he gives the scheme:



In this scheme the role of the methyl iodide as an active agent is not disclosed and is not understood. It appears in the scheme twice: the first time, apparently as a catalyst of the isomerization cycle, and on the second occasion as a methyl cation, adding on to the previously formed C-anion.

As a matter of fact, methyl iodide acts upon the enolate by the general acceptor-donor mechanism, itself being the acceptor agent, similar to the nitronium ion in nitration reactions, and to the chlorine ion in the chlorination of unsaturated compounds. The electron shift occurs at the moment of reaction and does not preceed it, as Chelintsev thinks [17]. The direction and course of the reaction are determined by the active agent and may be expressed by the scheme:



The reaction proceeds as a C-alkylation, and not as an O-alkylation, because the formation of a complex with a C-ring requires a smaller energy of activation than the formation of an O-ring. On the contrary, the methylation of aromatic enols (phenols) is assumed to proceed as an O-alkylation, because the formation of the complex in the ortho- or para-position to the hydroxy group would require a disturbance of the stability of the aromatic system.

It is only proposed that the scheme for the alkylation of acetoacetic ester includes both the electromeric effect of Nesmeyanov, and the isomeric cycles of Chelintsev. Together with these it describes the reaction as a real energetics necessity and as a process whose details are clear.

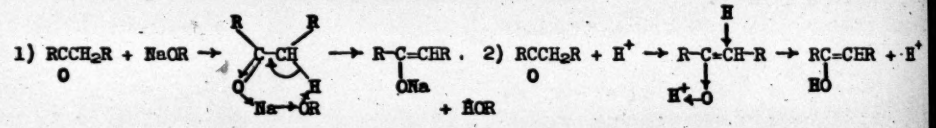
explanation and are not commented upon;[1] abnormal ones are the subject of detailed examination[2].

However, the duplexity or multiplicity of the reactions is a general property of organic compounds and is not in any way specific for quasicomplex compounds. In contemporary theories of organic transformations, the duplexity of reactions is in many cases connected with the nature of the reagent. In particular, the direction of the reaction of compounds of the chlorvinylmercury chloride type is determined by whether the agents belong to the classes of electron-donors (I^-, CN^-, $S^=$) electron-acceptors, (I_2, HBr, $IC1_3$) or of proton acceptors (KOH). They do not postulate anything exceptional or irregular in reactions, in which the entering group does not go into a site occupied by a substituent group, or when changes are produced within the molecule in atoms at locations other than that of the point of attack. It is illogical and inexpedient to name such reactions anomalous, even within the meaning of structural anomalies. Those "anomalous" cases, which Nesmeyanov chooses to cover by the principle of σ-conjugation, enter as particular cases in the general theory of organic conversions, within the framework of donor-acceptor mechanisms of addition and fission.

[1] But in fact their mechanism is at present less clear than that of the "abnormal" reactions, just as the mechanism of exchange reactions with conventional configurations is for us not as clear as is the mechanism of the "abnormal" Walden inversion.

[2] This relates, by the way, to the reaction of tautomeric substances, which have been the subject of polemics between Nesmeyanov and Chelintsev [3]. Both authors call C-alkylation abnormal, and O-alkylation normal. However, I am in complete agreement with Nesmeyanov's assertion that in C-alkylation the enolate is in no wise tautomeric. It is a chemical reaction which Nesmeyanov treats as a transfer of reaction centers, but for which I proposed a scheme, as set out above for the C-alkylation of acetoacetic ester.

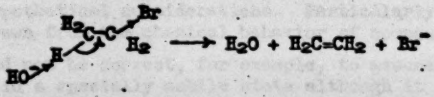
It may be added that in the very transition of one tautomeric form into the other, there is a "transfer of reaction centers" as can easily be seen from the following scheme of alkaline and acid enolization.



Tautomerization is not a process, but an equilibrium relationship of isomers between two compounds. It would be inexpedient to introduce into this concept any of the elements of the mechanism of organic reactions.

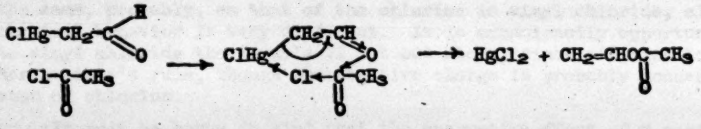
This is the place to observe that, as the theory stands at the present time, in my opinion, it is unnecessary to designate different forms of tautomers: desmotropes, allelotropes, merotropes, and pseudomers. It is sufficient to establish one term to designate the equilibrium mixture of isomers, and this term appears to be the widely used, though inexact, word "tautomer".

We find the picture of σ-conjugation if not in every, at least in many reactions forming double or triple bonds. The detachment of hydrogen bromide from ethyl bromide by the action of aqueous alkalies in no way differs, in principle, from the decomposition of chlorovinylmercury chloride:



However, the principle of σ-conjugation is difficult to apply to the case of the reverse reaction of addition. This is a serious gap in a theory which aims at the interpretation of chemical processes.

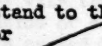
On the other hand, the absence of a suitable structure may exclude this or that general reaction. For example, β-chloromercurypropanal cannot react with acetyl chloride in the way that chloromercuryacetaldehyde reacts, forming vinyl acetate. The mechanism of this addition reaction, discovered in Nesmeyanov's laboratory [18], may probably be represented thus:



The inability of β-chloromercury propanal to react in the same way would, probably, be connected with the absence of σ-conjugation from its molecule.

But it is fairly clear, on the other hand, that such an inability of reaction for β-substituted propanal is conditioned by purely structural factors.

It seems to me that in the analysis of the mechanism of a reaction and of its energetics conditions, we find a deeper principle for this or that course of a chemical reaction, that in the pure idea of σ-conjugation.

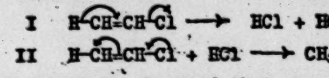
If it is acknowledged that σ-conjugation has an electromeric nature, then the question arises, in what relation does it stand to the mesomeric state of the molecule? Evidently, formulas  or

[19]

do not belong with certainty to the same molecule, in its unexcited state, while at any rate there is no indication that its mesomeric state corresponds to the electromeric one.

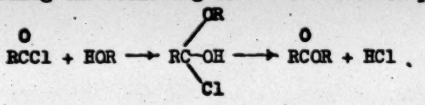
Since the electromeric formula is derived from reaction equations, it indicates the actual direction of movement of electrons at the time of the reaction. However, in different reactions, there may frequently be a different direction of movement of the electrons for one and the same compound. Thus, it is necessary to ascribe several electromeric formulas to each organic compound. Certain of these are in contradiction with the mesomeric formula, which, it is assumed should be unique for a given compound.

For example, two electromeric formulas must be assumed for vinyl chloride, corresponding to two of its typical reactions.



It should be observed that we are much more confident of the electromeric than of the mesomeric formulas. The mesomeric state is frequently based upon different hypothetical considerations. Particularly doubtful are the conclusions about it, drawn from the chemical behavior of compounds.[1)]

It would not be correct, for example, to assume that in acid chlorides the chlorine is in a specially mobile state although it is easily replaced in reactions with alcohols or amines. In actual fact, the activity of the acid chloride is conditioned by the proneness of the carbonyl compounds to addition reactions making the following course of reaction possible:



The actual state of the chlorine in the acid chloride is approximately the same, probably, as that of the chlorine in vinyl chloride, although their chemical behavior is very different. It is occasionally opportune to ascribe to vinyl chloride the formula II set out above, since addition to it follows Markovnikov's rule, though the negative charge is probably concentrated on the atom of chlorine.

It must be borne in mind that the energetics effect of σ-conjugationsis in many cases less in comparison with the energetics effect of chemical reactions. Markovnikov's rule applies so well not because in the molecule of unsymetrical olefins there is a certain (small) displacement of the electrons in the double bond, but because the reacting acceptor molecule more easily extracts an electron [1] It may be doubted, for example, whether in phenol and in analogous compounds there are higher electron densities simultaneously in the para- and in the two ortho-positions. There are no physical indications of this. As to the phenomenon of orientation which takes place in the presence of a reagent, at the moment of reaction an elevation of the electron density can occur at any of the quinogenic places on the benzene ring, at which the reagent enters into combination. Chelintsev's assertion that the uniform "displacement of electron cloud density in the benzene ring, ... never agrees with the true orientation" is unfounded [20]. Whatever may be the distribution of electrons in the unexcited molecule, orientation of the entering group is caused by the mechanism of the reaction, or more exactly – by the energy and entropy relationships in the possible transition complexes, which are not determined by the mesomeric state.

It may be remarked here that the displacement of the electron cloud under the influence of the substituent, which Chelintsev characterizes as the logical consequence of the theory of mesomerism [20], cannot reckon with serious contrary argument. The fact is that any displacement of the electron cloud in the benzene ring breaks its symmetry, and leads to the appearance of double bonds, that is to the formation of quinoid systems. It is not possible to speak of the uniform displacement of the electron cloud to one side or the other. I do not propose to defend the present theory of mesomerism with this consideration. However its critic ought not, apparently, to proceed in this direction, which was, in the case in question, that selected by Chelintsev.

pair from the ring, than from the chain of conjugated atoms. There are therefore frequent cases, where a sufficiently energetic reaction proceeds in a direction contrary to that of the mesomeric displacement.

The methodological fallibility of the theory of resonance is due to the fact that it gives a reason for connecting the course of chemical reactions to the superimposed structure of the initial organic molecule, and not with the form and energetics of the reacting complex.

The concept of electromeric σ,π-conjugation, into which the hypothesis of quasicomplex state was converted, does not tie itself closely to the mesomeric state of the unexcited molecule. This idea appears to be a considerable step forward. However a more general and active theory ought to include in its schemes and framework not only the structural peculiarities of reacting compounds, but also an examination of the processes of reaction.

SUMMARY

An analysis of the hypothesis of the quasicomplex state shows that the concept of quasicomplex compounds does not find a sufficient basis in the structure and properties of the compounds to which it is applied. Principally valency and complex compounds exist separately in the form of isomers and tautomers and do not remain in intermediate forms.

The reactions of the compounds called quasicomplex are covered by the general theory of donor-acceptor mechanisms, which includes the electromeric transfer of electrons, postulated by the quasicomplex hypothesis. There is no basis for separating reactions into normal and anomalous, since their duplexity or multiplicity is connected quite regularly with the different nature of the agents and mechanisms of reaction.

The electronic condition of organic molecules, still does not predetermine their chemical transformations. It is necessary to consider the nature of each reagent and the form and energetics of the transition complex.

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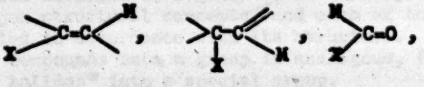
ANSWER TO E. A. SHILOV

A. N. Nesmeyanov

E. A. Shilov's paper is a conscientious and serious critical one, and I commence by expressing my thanks to the care which E. A. has spent on the study and criticism of my work. I cannot, however, agree with all that he has written.

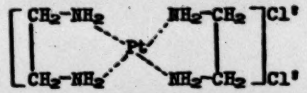
A number of metalloorganic compounds are obtained by addition of acetylenes, olefins, or carbon monoxide to mercury salts, and they are easily decomposed by various reagents, or by heating, with the liberation of acetylene, olefins, or carbon monoxide (free or combined in a mercury salt). Such a behavior gave rise to a lengthy discussion, in which one side proposed to relate these compounds to complexes of the Seitz type, (π-complexes, utilizing contemporary terminology) or to ammoniacal complexes of platinum derivatives. A number of pieces of work showed the incorrectness of this point of view, and established the structure of the type of substances in question, as products of the addition to double (or triple) bonds, or to the third and fourth valencies of carbon in carbon monoxide. Our work relates also to a number of recent investigations. I, R. Kh. Freidlina, A. E. Borisov, I. F. Lutsenko, N. K. Kochetkov and a number of our colleagues, carried out decisive tests to the advantage of the latter point of view, and finally deleted the mercury-organic compounds discussed (and also the Tl-, Sn-, Pb-, Sb-, I-compounds of this type first obtained by us) from the class of complexes, beyond any shadow of doubt. This is the heart of the matter. Hence for compounds of this type we proposed the name of quasicomplex. This name does not compare, but contrasts them with the complexes with which they were associated. Quasicomplex compounds of metals are compounds which, being constructed like metalloorganic compounds of the type:



do not possess the structure of complex compounds, but their behavior in a number of reactions is similar to that of complex compounds. Hence we showed that the term "quasicomplexes" is appropriate and descriptive. E. A. Shilov knocks at an open door in striving to show that quasicomplex compounds are not structurally similar to complex ones. But he asserts further, that in reactivity they are not similar to complex ones, that contemporary formulations of complex structures "do not contain the concept of instability".

We should like to ask why it was that the possibility of relating the group of metalloorganic compounds under discussion with complex ones, was discussed for a decade after the work of A. Werner. Evidently, the fact that their reactivity easily regenerates the original components induced many people to draw such a conclusion, among them being specialists in the field of inorganic complex compounds, such as Manchot. It may be noted that, notwithstanding the opinion of Shilov, actual complex compounds are characterized by an ease of regeneration of their components from them. Thus ethylenediamine can easily be extracted from ethylenediamine complexes, and ammonia ammoniates, etc. The whole chemistry of "introduction" is constructed on such expulsions. When the stability of a bond

in a complex compound is spoken of, this stability is contrasted with that of ionic bonds asserting, with justice, that ethylenediamine in



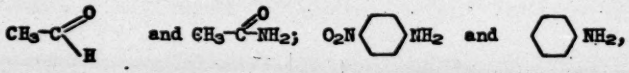
is bound to the platinum rather more closely than to the Cl ion. The ion bound to the complex loses its characteristic property.

Matters are otherwise when complex compounds are compared with, for example, typical organic compounds of covalent structure. In his well known book "The Electronic Theory of Valency", Ch. VII, dealing with complex compounds, Sidgwick [1] writes on p. 121 "the specific property, which the presence of a coordinate bond confers on the molecule, depends on two peculiarities; that this bond is more easily dissociated than the usual covalency...." Sidgwick reports further on the "ease, with which the product of addition (addition compound) is frequently dissociated with the formation of the original molecules." He further expounds the general property of complex compounds, that it is energetically more advantageous for their molecules to break down into fragments capable of independent existence, such as, for example, free radicals.

Thus, quasicomplex compounds have a characteristic similarity (of course, external) with complexes in reactions (but not in structure). This characteristic similarity was sufficient to justify the contrast, inparted by the prefix "quasi", in relation to structure. In order to underline still more the similarity of reactions (but an external "simulated" similarity) of quasicomplex and complex compounds, we call to mind that we demonstrated that the unsaturated component of a quasicomplex compound may, in a number of cases, be displaced and replaced by typical complex-forming substances (with $HgCl_2$), such as $Pb(C_6H_5)_3$, or even by other unsaturated compounds, a process externally similar to the reaction of "introduction" into the first sphere of the complex.

However, it may be argued that quasicomplex compounds are not a definite classified division of organic or metalloorganic compounds. Classification is based upon structural concepts, and each of the quasicomplex compounds can be classified in accordance with its structure. The role of uniting the quasicomplex compounds into a group is analogous, for example, to that of uniting "pseudo halides" into a special group.

However, the circumstance that we arrive at firm conclusions about the structure of β-metal-substituted alcohols and chlorovinyl quasicomplex compounds does not resolve, in my opinion, the question of their fine structural differences from alcohols, vinyl chloride, respectively. We refer to the fine structural differences which are similar to those observed in pairs of compounds such as:



ethylene and 1,3-butadiene and so on, and in general in those molecules which exhibit in a clear cut and well-known form the differing reactivities of the members of these pairs of compounds. We refer, therefore, to the mutual influence of atoms on molecules and of its nature - the mutual influence, which Butlerov considered to be an ineradicable part of the chemical structure of a compound. From a study of the reactions of quasicomplex compounds, and partially from their physical properties which, besides, have not been adequately studied, we attempted to go into the question of this fine structure. In the

course of this, as Shilov correctly notes, and as should be quite clear from our papers, our point of view underwent development. The primary attraction for me of the "theory" of resonance was doomed in advance, because (as was quite clearly established in the numerous discussions which ensued) the "theory" of resonance is defective in its physical foundations - the phenomenon of resonance structures does not occur in nature. This I have said publicly and have written in my papers [2].

I consider that, once the basis is acknowledged to be faulty, it is not necessary to examine all the following: the questions of "hybridization structures", of the "(statistical) weight of structures", or of such an idea as that of "federativity"; all these ideas fall together, and in this I agree with Shilov.

All the results of research lead us to the conclusion that the behavior of quasicomplex compounds (as also that of any other compound) is determined by the electromeric dynamic effect, and not by the static effect, polarizability, or by the polarization of the molecule. The use of this was gone into in our last paper, and more fully in my paper in the "Scientific Reports of Moscow State University" for 1950 [2]. It is not necessary to repeat all these considerations. We assume that the capacity of quasicomplex compounds for the electromeric displacement referred to - enhanced polarizability of the metal-C-C-X bonds (where X=halogen, OH, etc) - is a particularly strong expression of their structural peculiarities. As far as I understand it, this represents a unique point of disagreement between the opinions at which we have arrived, and the view developed by Shilov. The value of the reaction complex, (its structure and energetics) in the direction of the reaction seem to me quite clear. However both the structure and the energetics of the reaction complex cannot depend on the chemical structure of the reacting substance.

Shilov's critique is based on the proposition that I have not studied the mechanism of reaction, in particular the mechanism of the decomposition of quasicomplex compounds, taking into account the kinetics of these reactions and the assumed form and properties of the transition complex. That these factors (in the last analysis thermodynamic ones), as Shilov instructively points out, determine the direction of any reaction, is indisputable, so that there is thus no problem of the characteristic reactivity of quasicomplex compounds. I likewise assume that there is no special problem of the reactivity of quasicomplex compounds, that this is a general problem of reactivity, and that quasicomplex compounds are of interest, in that they are examples of especially sharp and clear-cut general regularities.

The following may be said about the mechanism of reactions which we did not study: Shilov does not see that, while the aim of his investigations has been to explain the mechanism of reactions, the aim of our work has been to explain the structure, and among them questions of the fine structure, of the compounds investigated. The whole of experimental organic chemistry confirms that the task of explaining the structure of compounds from their reactions is a real and decisive problem and, for its resolution, in the enormous majority or cases, a knowledge of the direction of the reactions of the substance investigated, under the influence of different reagents, is sufficient. This is justified and, in relation to questions of fine structure for example, reactions can clarify not only the position of double bonds, but also their (state of) conjugation, and may serve to assess more or less the degree of conjugation.[1]

[1] The difficulties encountered in purely chemical means of research relate only to the differences of static and dynamic factors of conjugation.

Structures have been established for many hundreds of thousands of organic compounds, but the kinetics and the mechanism of reaction of comparatively few of them have been studied.

The indisputable thermodynamic and kinetic considerations expressed by Shilov can easily be understood to lie on other (not structural) planes of the question. It would have been possible to use them at will, with like success, in the attempt to uncover the structure of any compound. For what reason should the structure of a compound such as C_2H_6O be discussed in relation to its conversion to ethyl chloride with PCl_5, to vinylsulfuric acid with H_2SO_4, and to sodium ethylate with sodium, etc., when it is clear that the direction of these reactions is conditioned only by thermodynamic and kinetic factors and depends every time on the reagents with which the substance reacts, and when it is sufficient to know these factors in order to predict the reactivity without any structural formula. The search for structural causes of the capacity of a substance for any reaction in no way runs counter to the thermodynamic and kinetic conditioning of these reactions. Therefore I cannot in any way give up the question of the searches for specific lines of chemical structure, responsible for a complete large characteristic group of reactions of a given type of compound, on the basis that these reactions are conditioned by thermodynamic and kinetic factors. Shilov rightly gives a lot of attention to the question of the structure of the reaction complex. In my opinion, the structural chemistry of the transition state (not speaking yet of its energetics) is one of the most important problems of chemistry among those which are awaiting their turn for solution. However, it must be admitted that at present rather unreliable assumptions are made about the structure of the transition state on the basis of a knowledge of the structure of the initial compounds, while the reverse procedure is rarely resorted to. Perhaps it is possible to use for example, those forms of the transition complexes set out by Shilov in his paper [3], as a somewhat more than working hypothesis, useful for setting up experiments, but still sufficiently theoretical. And perhaps from this theoretical structure it may be possible to draw conclusions about the structure of reacting substances, and not the contrary.

The second general observation concerns the question which Shilov raises as to the incorrectness, in his opinion, of my use of the expressions "normal" and "anomalous" reactions. The matter is not merely one of terminology. The observation is more general, I think, because here also Shilov starts out from natural modes of reasoning, based on synthetic and structural chemistry. Shilov would have been right, if the words "normal" and "anomalous" were customarily used with the meanings of "natural" and "unnatural". It is obvious that every original reaction is natural and in this sense is normal. However more common, more characteristic and, mainly, of more decisive importance for organic chemistry as a science, are those exchange reactions RX + PY → RY + PX, in which the residue Y entering the molecule RX goes into the place rendered vacant in the molecule by the residue X. This brings in the principle known as that of the smallest structural change. If a large portion of reactions did not follow this principle, the derivation of structural formulas and the construction of the present edifice of organic chemistry would have been impossible.

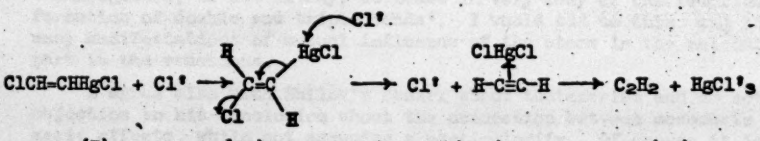
Where this principle is infringed (as in the chemistry of terpenes), the derivation of structures is extremely difficult. That is why rearrangements are so diligently studied in organic chemistry. That is precisely the reason for the preeminence of the founder of the theory of structure, A. M. Butlerov, of the chemists of his school, and of his direction of many studies made in the field of rearrangements. That is why any reaction, in which the entering substituent does not go into the place vacated in the molecule by the residue or atom which

is exchanging with it, is anomalous in the view of organic chemists, although it is self-evident that any reaction, once it starts, is normal from the point of view of thermodynamics. It is opportune to say that it is in vain for my opponent to bring up the Walden inversion. He refers to the configuration of the conversion, but structurally the substituent goes into the place vacated by the atom or residue.

This is how the matter of "normal" and "anomalous" reactions stands. I now have little space left to devote to the question of the multiplicity of reactions. Would it be disputed that every compound is capable of a multiplicity of reactions? But it is necessary to find order among this multiplicity. Then some predominant reactions are brought up. And the reason for these is sought mainly in the structure of the molecule. Thus C_2H_6O is capable of many reactions - combustion yields water and CO_2; passage over many rare earth oxides yields acetaldehyde, then acetic acid; with PCl_5 ethyl chloride is formed; with Na, the alcoholate and so on. But a considerable number of these reactions are conditioned by the presence of the hydroxyl group and a chain of two carbon atoms in the compound, i.e. are predetermined by the structural factors of the given molecule, which does not of course exclude, but assumes, an influence of the reagent, suitable for the development of the given structural factors in the reaction. Thus also stands the matter of fine structural differences. 1,3-Butadiene is capable of many reactions. But a number of these manifest conjugation in the 1,3-double bond, Acetaldehyde, chloromercuryacetaldehyde are capable of a variety of reactions. But many of these evidence the special property of "mobility" of the α-hydrogen and correspondingly of the α-mercury atom, the latter in higher degree than the former. Likewise in many of the reactions of ethanolmercury chloride, out of all those possible, the detachment of ethylene is incomparably easier than it is, for example, from ethanol. In order to convince oneself of the sharpness of this difference in behavior, it is sufficient to subject the two compounds to the action of dilute acids at room temperature (and not only to the action of KI or $Na_2S_2O_3$), i.e. to direct an electrophilic attack on the hydroxyl.[1] In the first case there is a quantitative liberation of ethylene, whereas with ethanol nothing at all happens. In my paper which has been cited [2], I put forward considerations as to why I considered it probable that in all the examples given there should be more or less pronounced conjugation of the bonds (σ−σ and σ−π), in many of them similar to the generally acknowledged conjugation of double bonds.

The reproach which Shilov administers to me for my inattention to the properties of the reagent and the character of the reaction, I cannot accept. Frequently in our work we speak of the action of concrete reagents, the direction of attack of which is evident. The only thing that is true is that we do not make special assumptions about the structure of the transition complex. The above explains why.

In the equation, presented by Shilov:

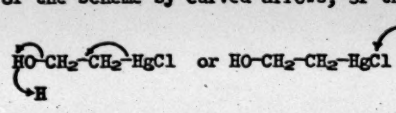


(I) (II) (III) (IV)

only III, the π-complex stage, appears novel, and this is proposed by Shilov on the basis that the measured velocity of similar addition reactions with multiple bonds discloses the participation in the reaction of a third molecule, and the deviation of the reaction from a bimolecular course. It is possible that this contention is justified. It is in any case not doubted that a knowledge of the kinetic of a reaction is a first step towards the explanation of its mechanism.

[1] E. A. Shilov compares incomparables: the absence of action of acids on chlorovinylmercury chloride and their dehydrating action on alcohols.

Stage II, of course, always enters into our schemes. We always assumed (and it is impossible to conceive any other interpretation) that a nucleophilic reagent binding mercury into the complex, and decomposing (in the case given) with elimination of acetylene, attacks the mercury atom, and in no case attacks any other part of the molecule, a state of affairs only expressed by stage II in Shilov's scheme. Although I do not see any objections to the hypothetical π-complex stage in the reaction scheme, I must remark that it is not at all necessary in order to arrive at the conclusion that Cl^- facilitates synthesis of chlorovinylmercury chloride. For this it is sufficient to establish that the reaction $ClCH{=}CHHgCl + Cl' \rightleftarrows C_2H_2 + HgCl_3'$ is reversible, and that free $HgCl_2$ reacts with acetylene in the opposite direction. It is a peculiarity of our viewpoint that the electronic displacement, designated in stage II of the scheme by curved arrows, or the displacement equivalent to it



proceeds as easily in diverse reactions because the system of bonds HO-C-C-Hg, O=C-C-Hg and Cl-C-C-Hg has an enhanced polarizability, compared, let us say, with the system HO-C-C-H, O=C-C-H or Cl-C-C-H. This is a conclusion concerning a definite structural property of the given molecule. I do not see that this would be doubted by my opponent. To say that "apparently (! A. N.) the polarizability will always be sufficient for decomposition if the energetic relationships, both in thermodynamics and kinetics, suffice for the corresponding reaction" is another way of saying that the polarizability is always sufficient when it is sufficient.

I also imply a different result of the attack of the hydrogen ion on ethanol and on ethanolmercury chloride. It may be added that without elimination of the mercury, the hydroxyl group is more easily detached from ethanolmercury chloride than from ethanol. Thus ethanolmercury chloride is quite easily converted to β,β'-dichloromercuryethyl ether by the dehydrating action of acetamide. In trans-chlorovinylmercury chloride the mercury atom is, in a high degree, more "exchangeable" (in reactions with metallic salts) than in aliphatic or aromatic mercury-organic compounds. Thus, this mutual influence of the mercury atom and the chlorine or hydrogen atom in the β-position to it is exhibited quite graphically.

It is beyond doubt that the systems with very pronounced conjugation (π- or π-σ) are not divided by a wall from systems in which the conjugation is less pronounced. I can only agree that "those cases, which Nesmeyanov chooses to embrace with the principle of σ-conjugation, enter as special cases into the general theory of organic transformations" and that "we find the picture of σ-conjugation, if not in any, at least in very many of the reactions involving formation of double and triple bonds". I would add to this and likewise in many manifestations of mutual influence of the atoms in the molecule, taking part in the reactions.

I agree also with Shilov's remark about tautomerism and do not have any objection to his conclusion about the connection between mesomeric and electromeric effects, while not assuming a particularity. Of course it is scarcely possible in all cases to examine the mobility of the halogen of the acid halides, and in many cases this may even be the result of previous addition of reagent to the double bond of the carbonyl group. However this has no relation to the essential question under discussion.

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[1] Sidgwick. The Electronic Theory of Valency. Oxford (1927).

[2] A. N. Nesmeyanov, Scientific Reports of Moscow State University, No. 132. Organic Chemistry Vol.7, p.5 (1950); and likewise the subsequent papers in the same volume.

[3] E. A. Shilov, Proc. Acad. Sci. USSR 18, 643 (1938)

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...ION OF SILICOTUNGSTATES BY HYDROGEN, p. 2155

...g. 1. X-Ray diagram of standard sodium bronze.

...g. 2. Crystals of sodium ...icotungstate.

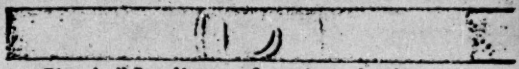


Fig. 3. X-Ray diagram of specimen of sodium silicotungstate reduced at 500°.

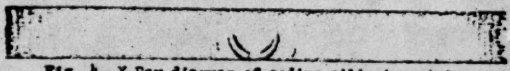


Fig. 4. X-Ray diagram of sodium silicotungstate reduced at 600°.

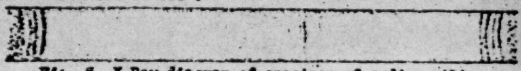


Fig. 5. X-Ray diagram of specimen of sodium silicotungstate reduced at 700°.

Fig. 6. X-Ray diagram of specimen of sodium silicotungstate reduced at 800°.

COMPLEX COMPOUNDS OF SOME BIVALENT METALS WITH ANTIPYRINE, p. 2183

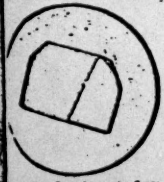
Appearance of crystals under microscope x 120.

...g. 1. $[Cd(Ant)_2](CNS)_2$, ...d crystallization.

Fig. 2. $[Cd(Ant)_2](CNS)_2$, slow crystallization.

Fig. 3. $[Zn(Ant)_2](CNS)_2$.

Fig. 4. $[Zn(Ant)_2]Cl_2$, rapid crystallization.



...g. 5. $[Zn(Ant)_2]Cl_2$, ...crystallization, ...e crystal.

Fig. 6. $[Zn(Ant)_2]Br_2$ rapid crystallization.

Fig. 7. $[Zn(Ant)_2]Br_2$, slow crystallization.

Fig. 8. $[Cd(Ant)_2]Br_2$ rapid crystallization.

...g. 9. $[Cd(Ant)_2]Br_2$, ...crystallization.

Fig. 10. $[Zn(Ant)_2]I_2$, ...apid crystallization.

Fig. 11. $[Zn(Ant)_2]I_2$, slow crystallization.

Fig. 12. $[Cd(Ant)_2]I_2$.